

Concentrations, Distribution, and Persistence of Perfluoroalkylates in Sludge-Applied Soils near Decatur, Alabama, USA

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Sludges generated at a wastewater treatment plant (WWTP) in Decatur, Alabama have been applied to agricultural fields for more than a decade. Waste-stream sources to this WWTP during this period included industries that work with fluorotelomer compounds, and sludges from this facility have been found to be elevated in perfluoroalkylates (PFAs). With this knowledge, the U.S. Environmental Protection Agency collected soil samples from sludge-applied fields as well as nearby “background” fields for PFA analysis. Samples from the sludge-applied fields had PFAs at much higher concentrations than in the background fields; generally the highest concentrations were perfluorodecanoic acid (e 990 ng/g), perfluorododecanoic acid (e 530 ng/g), perfluorooctanoic acid (e 320 ng/g), and perfluorooctane sulfonate (e 410 ng/g). Contrasts in PFA concentration between surface and deeper soil samples tended to be more pronounced in long-chain congeners than shorter chains, perhaps reflecting relatively lower environmental mobilities for longer chains. Several PFAs were correlated with secondary fluorotelomer alcohols (sec-FTOHs) suggesting that PFAs are being formed by degradation of sec-FTOHs. Calculated PFA disappearance half-lives for C6 through C11 alkylates ranged from about 1 to 3 years and increase with increasing chain-length, again perhaps reflecting lower mobility of the longer-chained compounds.

Introduction

For a little over a decade, a wastewater treatment plant (WWTP) in Decatur, AL has been permitted to apply sludge it generated on about 2000 ha of local agricultural land. Waste

stream to this WWTP varied during this time, but are known to have included effluents from industries that conducted electrochemical fluorination and fluorotelomerization, as well as industries that worked with a variety of fluorotelomer compounds (FTCs) and perfluoroalkylates (PFAs). When sludges from this WWTP were analyzed for FTCs and PFAs they were found to be elevated relative to other sludges (see Supporting Information (SI); 1, 2). These elevated levels generated concern that the Decatur sludge applications might constitute an exposure route because application of sludges having high PFA to soil has been documented to contaminate surface and drinking waters (3). Consequently, these elevated concentrations in the Decatur sludges spurred prudent efforts to decrease PFA loads to the WWTP, and sludge PFOA concentrations generated at the facility have fallen off dramatically since 2006 (Figure SI 1). With this as background, in an effort to evaluate the impact of the sludges that had been applied to the Decatur fields, in late 2007 the U.S. Environmental Protection Agency (USEPA) collected and analyzed a small number of sludge and soil samples from fields that had received some of the highest sludge loads. These results documented the presence of high concentrations of several fluorotelomer alcohols (FTOHs) and PFAs in soils of the land-application areas.

The USEPA subsequently collected (November 2008) and analyzed water samples from a few Decatur, AL public drinking-water supplies. No levels of the perfluorooctanoic acid (PFOA) or perfluorooctane sulfonate (PFOS) were observed above the Provisional Health Advisories of 0.4 µg/L for PFOA and 0.2 µg/L for PFOS (4) in these municipal drinking-water samples. In February 2009, the USEPA collected additional water samples from selected private wells, agricultural ponds, and other surface waters located in and immediately around the land-application fields (5). Some of these samples were found to have PFA levels exceeding the Provisional Health Advisories.

An expanded set of surface and subsurface soil samples was collected in March 2009 to characterize the extent and magnitude of the PFA contamination in the land-application area. The general results of these efforts have garnered considerable attention in the lay press (6, 7), but the actual data have yet to be reported before now. In this paper, we report the analytical methodologies employed, the analytical results for both the 2007 and the 2009 surveys, and examine these data for patterns that illuminate the fate of these compounds. In a companion paper (8), we report analytical results for FTOHs, which have been shown to degrade to form some of the perfluorocarboxylates (PFCAs) we report here.

Materials and Methods

Sample Collection. Decatur, AL region soil samples were collected by USEPA regional scientists from (i) 2 sludge-applied fields and 1 sludge-free background field in September 2007; and (ii) 6 sludge-applied fields and 1 sludge-free background field in March 2009. One of the sludge-applied fields, 09H, received only one sludge application in the distant past. All sampled fields were in pasture; we plan to report upon an analysis of grasses from these fields in a future paper. Table SI 1 in the SI lists the sampled fields, documented sludge-application history, sample-identification numbers, and descriptions for the soil samples, and Figure 1 depicts the sampling locations.

The sampling equipment, composed of stainless steel, was washed three times with Optima-grade methanol (MeOH) prior to use. The samples were stored in certified-

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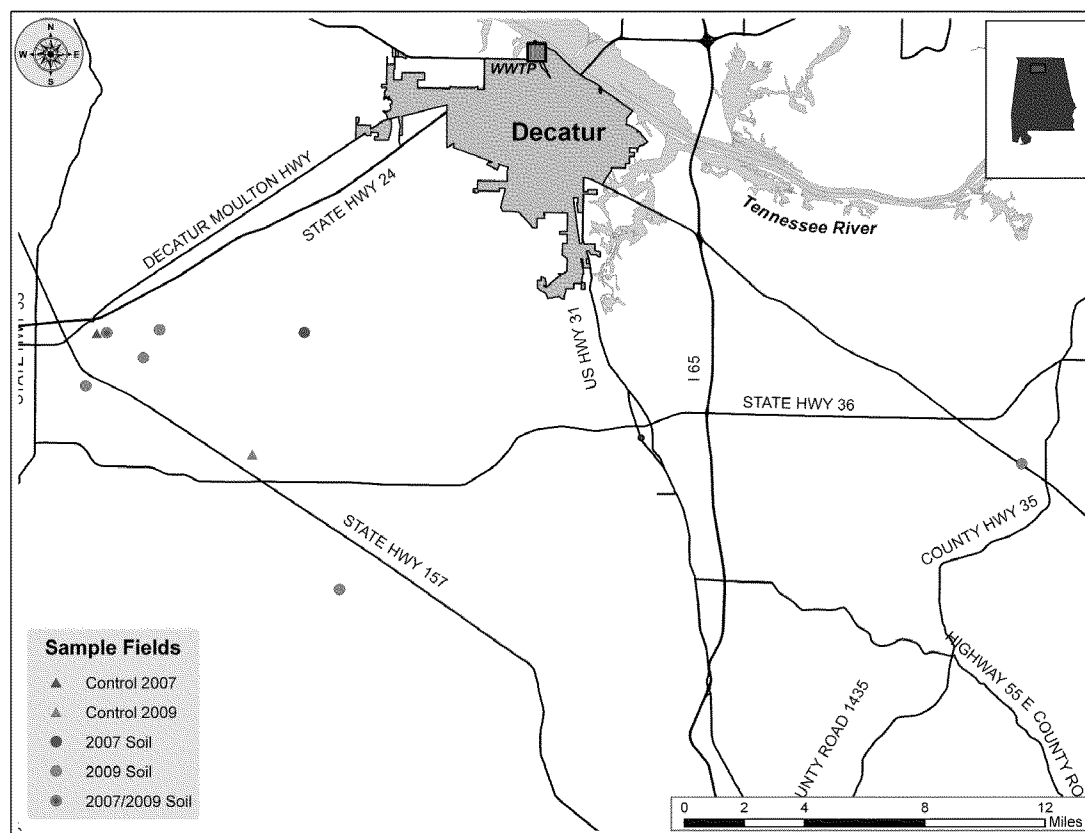


FIGURE 1. Sample locations for this study are south, and within an approximately 20-mile radius, of Decatur. Field numbers are not designated in the interest of preserving confidentiality regarding PFA concentrations of individual properties.

clean 500-mL, wide-mouth high-density polyethylene (HDPE) containers. The sampling equipment and containers were determined to be free of contamination for the intended analytes before the sampling trip by rinsing a representative of each item type with 60/40 (volume/volume) acetonitrile/water (ACN/H₂O) and analyzing the rinses. Surface-soil samples were collected from the 0- to 10-cm interval using sampling spoons, hand augers, and pans. Subsurface-soil samples were collected by Geo-probe from intervals bounded between the 23- to 56-cm and the 152- to 165-cm depths (Table S11).

Quality-control sample taken to the field included Ottawa sand that has been shown to bear low concentrations of target analytes and a commercial top soil, the Cowart soil, for which the general range of concentrations of a variety of analytes has been documented to be low as well (9, 10). Also, duplicate field samples were collected from selected locations in the sludge-applied fields.

Chemicals. All chemicals used in this study were of the highest purity offered by the suppliers, uniformly ≥97% purity. We identify the chemicals we used in the Supporting Information.

Sample Preparation and Extractions. Field-moist samples from the 2007 sampling ground were sieved through a MeOH-washed, 2-mm, stainless-steel sieve and extracted in triplicate. Because these samples yielded a high degree of variability in [FTOHs] between aliquots drawn from the same sieved sample (9), the 2009 sampling-round samples were homogenized by repeatedly passing them through 2-mm, stainless-steel sieves, coning and quartering until the sample was reduced to four approximately 1-g aliquots. Each of the four aliquots was transferred to a precleaned, labeled 16-mL polycarbonate (PPCO) centrifuge tube and sealed with a PPCO press-on cap; two of these aliquots were extracted for the PFA analyses reported herein and the remaining two were extracted for FTOH analyses which are reported in our

accompanying paper (8). In addition, aliquots were removed from all samples to measure moisture content, by drying, which was used to calculate the concentrations reported herein on a dry-weight (dw) basis from the extractions which were performed on moist soils.

We extracted the 2007 and 2009 samples using different methods, but each was optimized for these sludge-applied soils as described below. For the 2007 samples, we performed an extraction designed to recover both PFAs and FTOHs from the same aliquot (11). We optimized this method for sludge-applied soils by extracting one sample seven times with MTBE to determine the number of steps necessary to balance satisfactory recoveries against diminishing returns with additional extraction steps. Based on this, we extracted the 2007 soils with four MTBE extractions in sequence, which we pooled for analysis, followed by an ACN extraction in accordance with the procedure described in our earlier paper (11). For the 2009 surface-soil samples we extracted the PFAs and FTOHs from separate aliquots drawn from each sample. For the PFAs, we used a modification of an ACN/H₂O extraction we reported upon earlier (10). Based upon exploratory efforts with a few sludge-applied samples from our 2007 survey, we deviated from our published ACN/H₂O extraction method for uncontaminated soils (10) by extracting these sludge-applied soils four times with 60/40 ACN/H₂O, which we pooled for analysis, but otherwise following our published method (10). Although we modified our extractions of these surface-soil samples as described above to accommodate their PFA-contaminated nature, we retained all other practices from our published methods (10, 11) including (i) spiking samples prior to extraction with ¹³C₈-PFOA as a recovery internal standard; (ii) subjecting extracts to ion-pairing cleanup to decrease analytical noise from natural organic matter that normally is concentrated in surface soils; (iii) reconstituting extracts in 60/40 ACN/H₂O with a suite of mass-labeled PFAs (Table S13) present at 84 pg/g matrix

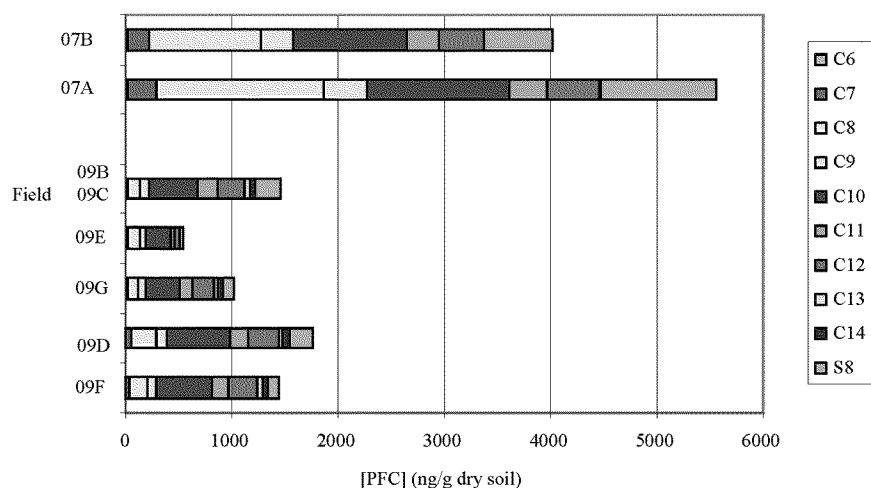


FIGURE 2. Geometric-mean surface-soil concentrations of analyzed PFAs within sampled fields. Results for the top two fields, 07A and 07B, are from the 2007 sampling campaign ($n = 4$ for 07B, $n = 3$ for 07A). The lower five fields are from the 2009 sampling campaign; fields 09B and 09C are contiguous and grouped together for this figure because they have similar sludge-application histories and only 3 samples between them ($n = 5$ for all other 09 fields).

internal standards; and (iv) running procedural blanks in which the extraction process was carried out on otherwise-empty extraction tubes. Additionally, we fortified selected samples from the 2009 campaign as a check of our analyte identification and quantitation.

Upon extraction of the 2009 samples, we discovered that all the subsurface soils exhibited poor returns of our mass-labeled recovery standard, $^{13}\text{C}_8$ -PFOA, in contrast to satisfactory recoveries for all the surface soils. With exploration, we discovered that the relatively clay-rich subsurface samples tended to cohere into poorly permeable pellets when shaken on the Eberbach shaker table. When we performed the extraction again on the subsurface samples, replacing the shaker-table step with end-over-end rotation on a Labquake rotisserie, the subsurface soils did not pelletize and the $^{13}\text{C}_8$ -PFOA recoveries fell in the satisfactory range as reported in the Results section. Because the subsurface soils were relatively low in natural organic matter, we found we could exclude the ion-pairing cleanup step on these samples with no deleterious effect.

Liquid Chromatograph, Tandem Mass-Spectrometer Analyses. Acetonitrile/water extracts were analyzed on a Waters Acquity ultraperformance liquid chromatograph (UPLC) interfaced with a Waters Quattro Premier XE tandem mass spectrometer operated in negative electrospray-ionization mode. Analytical methods are detailed in the Supporting Information along with an example of analytical results for an extract of a sludge-applied surface soil (Figure SI2).

Results

Data-Quality Metrics. In the Supporting Information, we report quality data reflecting on the field aspects of this study including (1) blanks and reference soils taken to the fields; (2) background-field samples; and (3) duplicate samples collected in the field. There were no anomalies among these metrics, except for the subsurface samples from the background fields (SI). These background subsurface samples returned detections for C6, C7, C8, and PFOS of about 4 orders of magnitude greater than their corresponding surface samples suggesting the possibility of low-level contamination of the subsurface sampling equipment for these analytes. For C6, C7, and C8, these detections still were an order of magnitude less than the detections in the sludge-applied fields, but PFOS was present in the background subsurface sample at about the same level as for the sludge-applied subsurface samples.

Quality data reflecting laboratory aspects of this study include (1) method blanks in which the extraction procedure was carried out in otherwise-empty tubes; (2) standard-curve back prediction; (3) recovery internal standards; and (4) standard additions to selected samples. All of these metrics indicate that the data in this study are of high quality (SI).

Results of Sampling in Sludge-Applied Fields. Analytical results for the samples from sludge-applied fields are tabulated in Tables SI9 for the 2007 survey and SI10 for the 2009 survey, and the average results for each field are depicted in Figure 2. For the 2007 survey, in fields 07A and 07B, the mass concentrations of analyzed PFAs sum to about 4–6 $\mu\text{g/g}$ dry soil (Figure 2). In contrast, for the fields sampled in 2009, except for field 09H, mass concentrations of analyzed PFAs sum to only about 0.5–2 $\mu\text{g/g}$ (Figure 2). Field 09H, which received only one sludge application in the distant past, had even lower PFAs, summing to $<10\text{ ng/g}$ (Table SI10). Surface soils were sampled twice in each survey for one field, field B; while the number of samples is small, these data also show lower values in 2009 than 2007 (Figure SI3).

Considering all the data in whole, the dominant analyzed PFAs generally include PFDA (C10), PFOA (C8), and PFOS (S8), followed by PFDoA (C12), then PFUnA (C11), and PFNA (C9) (Figure 2). With the exception of PFOS, the analyzed perfluorosulfonates mostly were not detected. None of the unsaturated fluorotelomer acids were detected in either the 2007 or the 2009 survey. For the 2007 survey, the maximum analyzed concentrations (ng/g) of these dominant species were [C10] > 2100 , [C8] > 2500 , [S8] > 1400 , [C12] > 1200 , [C11] > 690 , and [C9] > 650 (Table SI9). For the 2009 survey, however, the maximum analyzed concentrations (ng/g) of these dominant species were lower: [C10] > 140 , [C8] > 320 , [S8] > 410 , [C12] > 530 , [C11] > 310 , and [C9] > 140 (Table SI10).

Discussion

These analytical results document that the majority of the Decatur soils in the sludge-application areas have concentrations of numerous PFAs well above background levels. Here we examine these data for patterns with respect to time, space, and precursors.

Sources of Variation in the Data: Sludge-Application Rate and Time Since Application. A simple visual-scan comparison of the 2007 and 2009 surface-soil data (Tables SI9 and SI10) reveals large general differences in PFA levels

TABLE 1. First-Order Disappearance Constants and Half-Lives Modeled from Surface-Soil Data

PFA homologue length (C no.)	PFA F statistics ^a		disappearance rate constant, half life			
	sludge app. rate	time since app.	supported ^b		unsupported ^c	
			<i>k</i> (yr ⁻¹)	<i>T</i> _{1/2} (yr)	<i>k</i> (yr ⁻¹)	<i>T</i> _{1/2} (yr)
6	12.26	31.56	1.04 (0.32)	0.7		
7	29.16	70.00	0.81 (0.25)	0.9		
8	23.83	64.09	0.71 (0.30)	1.0	0.78	0.89
9	21.72	26.96	0.44 (0.25)	1.6		
10	19.86	14.76	0.37 (0.14)	1.9	0.53	1.31
11	36.34	4.48	0.25 (0.21)	2.7		
12	28.56	2.57				
13	48.01	1.84				
14	20.35	1.17				
8 (PFOS)	73.50	26.97	0.57 (0.15)	1.2		
Crit. F (0.05)	4.26	4.21				
Crit. F (0.01)	7.82	7.68				

^a F statistics from analysis of variance to test whether variation among sample (*n* = 31) sludge application rates (7 application rates) or a linear-functional model through time (4 time increments) explains a significant component of variation relative to among samples sharing a common sludge-application rate or time since sludge application. Bolded F values are significant at *p* < 0.01 and italicized values are significant at *p* < 0.05. See text for details. ^b Supported values characterize disappearance rates of PFAs that likely are being generated by degradation of their precursors, e.g., sec-FTOHs. ^c Unsupported values are estimates of disappearance rates in the absence of being generated by precursors. See text for details.

between the two surveys, with analytes being generally higher in the 2007 survey than the 2009. There are numerous possible causes for these differences including variation of PFA concentrations between batches of sludge applied to the fields, variation in sludge-application rates between fields, elapsed time between sludge application to the fields and soil sampling, and variation of soil physical or chemical properties among fields.

Evaluation of the contribution of temporal variation in sludge [PFA] to data set variance is limited because we have analyses of only a few Decatur sludge samples (Figure SI1); however, all the sampled fields received sludge during the years in which the anomalously high sludge [PFOA] values were recorded, specifically 2002 through 2006 (SI discussion, Figure SI1 and Table SI1).

The effect of "sludge-application rate" and "elapsed time between sludge application and soil sampling" on the data variance can be evaluated independently so long as these two variables are not correlated; Figure SI4 illustrates the absence of a statistically significant relationship between these variables, so the effect of each on soil [PFA]s can be evaluated. "Elapsed time between sludge application and soil sampling" might factor in data variance because increasing time offers the opportunity for numerous processes to act on the PFAs in the sludge-applied soils, potentially including: (1) uptake into plants; (2) erosive overland flow with precipitation events; (3) leaching through the soil column; (4) ingrowth from FTOH, and perhaps higher-order, precursors; and (5) degradation. If one or more of these processes controls a large part of the total variation in these data, then plots of PFA concentration vs time elapsed between sludge application and soil sampling might exhibit temporal trends. Homologous [PFCA]s are plotted in Figure SI5, and [PFOS] are plotted in Figure SI6, as a function of both "sludge-application rate" and "elapsed time between sludge application and soil sampling". Because these data are not bivariate-normally distributed, they cannot be statistically evaluated with simple correlation coefficients so we used an analysis of variance for unequal repeated measures (12). Table 1 presents a statistical summary of these plots. Figure SI5 and Table 1 reveal an interesting pattern wherein surface-soil [PFCA]s have a stronger statistical relationship (i.e., greater F statistic) with (1) sludge-application rate than elapsed time for the long-chain homologues; and (2) elapsed

time between sludge application and soil sampling than for sludge-application rate for the short-chain homologues. Among possible causes for this pattern is that environmental mobility decreases and/or recalcitrance increases with increasing homologue length.

Given these data as well as those of our accompanying paper (8), we can inspect the data for evidence of whether leaching through the soil column and/or ingrowth from precursors might play a role in the temporal variability of the short-chain PFAs observed in these soils.

Depth Profiles. Soil samples were collected from up to three depths, i.e., the surface, ~50 cm, and ~150 cm, at each of three locations in two contiguous sludge-applied fields, 09B and 09C (Table SI10) and the background field, 09Bg (Table SI6). Numerous PFAs were detected in the subsurface samples at all three sludge-applied sample locations (Table SI10), albeit, generally at lower concentrations in the deep soils than at the surface (Figure 3). When the concentration ratios of the mid-depth (~50 cm) to the surface and deep (~150 cm) to the surface are plotted as a function of chain length, a regular pattern emerges for all three sample locations wherein the subsurface/shallow ratios increase with decreasing chain length (Figure 4a and b). This pattern suggests that at least part of the reason that short-chains exhibit statistical decreases through time but long-chains do not (Table 1; Figure SI5) is preferential leaching of the short-chain congeners.

[PFCA] as a Function of [FTOH]. Wang et al. (13) has shown the 7:2 sec-fluorotelomer alcohol (7:2sFTOH; CF₃(CF₂)₆CH(CH₃)OH) to be a degradation product of the 8:2 primary fluorotelomer alcohol (8:2nFTOH; CF₃(CF₂)₇-CH₂CH₂OH) and proposed the degradation sequence of 8:2nFTOH → 8:2fluorotelomer aldehyde → 8:2fluorotelomer acid → 8:2 fluorotelomer unsaturated acid → 7:2sFTOH → PFOA. Following this logic, Ellington et al. (9), detected homologues of 7:2sFTOH, i.e., 9:2s, 11:2s, and 13:2sFTOHs, in a limited survey of Decatur sludge-amended soils. In our accompanying paper (8), we show a statistically significant functional dependence of the s-FTOHs on their n-FTOH precursors, suggesting that the longevity of the s-FTOHs is supported by degradation of their n-FTOH precursors. In Figure 5, we plot [PFCA]s as a function of both their n- and s-FTOHs. The PFCA is significantly related to their s-FTOH precursors for PFOA, PFDA, and PFDoA, but not PFTeA. In

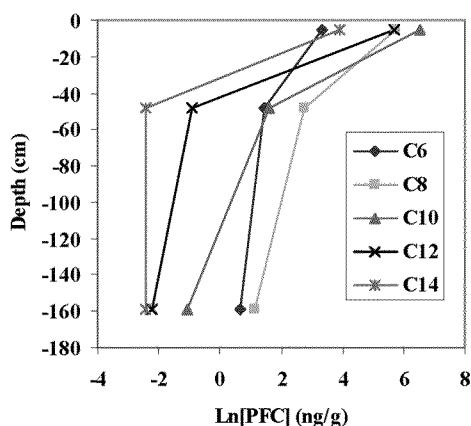


FIGURE 3. [PFA] (ng/g dry soil) vs depth for samples 09B3-1, 09B3-2, And 09B3-3. [PFA]s are transformed to the natural logarithms to facilitate depicting the wide concentration ranges among homologues and depths; nondetects are depicted at their limits of quantitation, also to ease depiction. With a few exceptions (Table SI10), analyte concentrations generally decrease or remain about the same with increasing depth. While only even-numbered PFCAs are depicted here, this relationship generally holds for odd-numbered PFCAs as well as PFOS (Table SI10).

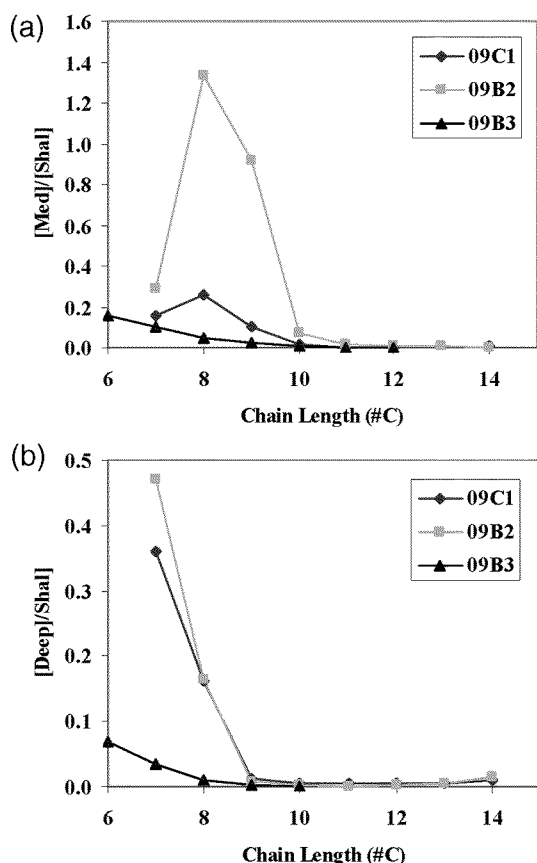


FIGURE 4. (a) [PFA] ratio (mid-depth/surface) at three sample locations. (b) [PFA] ratio (deep/shallow) at three sample locations. See text for discussion.

contrast, the PFCAs are correlated to their more remotely related *n*-FTOH precursors only for PFOA and PFTeA. The R oxidation of *n*-FTOHs to form odd-numbered PFCAs also has been identified as a minor biotransformation pathway (14); for this process, only 8:2*n*FTOH f PFNA exhibits a statistically significant relationship (Figure SI7). Taken as a group, these observations of significant relationships between some PFCAs and FTOHs supports the idea that part of their

persistence in the sludge-applied soils is due to ingrowth from FTOH degradation.

Disappearance Half-Lives. Based on the observations presented above, at least part of the declines in short-chain [PFA]s through time (Figures SI5 and SI6) reflect a balance between losses from leaching (Figure 3), and perhaps other depletion processes, that are offset by growth from *s*-FTOHs (Figure 5). While these processes commonly are modeled as first-order in the reactant (15), other more complicated factors might be at play as well. In the absence of evidence supporting such scenarios, however, we have modeled these losses as simple first-order. Nevertheless, it is important to realize that this modeling approach could significantly understate the persistence of these compounds in soil should more complex processes be active.

Supported Disappearance Half-Lives. The simplest first-order characterization of [PFA] loss through time reflects the effect of *support* by ingrowth from the chemical precursors, *s*-FTOHs, and the slope of linear regressions in $\ln[PFA]$ - time space yields estimates of supported first-order disappearance constants (k_{PFA}^s):

$$\ln[PFA] = \ln[PFA]_0 - k_{PFA}^s t \quad (1)$$

where $[PFA]_0$ equates to a statistical estimate of the PFA initial concentration when the sludge just has been applied. In turn, supported disappearance half-lives ($T_{1/2}^s$) for these compounds in the field that have received applications of sludge containing these compounds can be calculated according to

$$T_{1/2}^s = \frac{\ln 0.5}{-k_{PFA}^s} \quad (2)$$

Supported first-order disappearance constants and half-lives of our analytes are tabulated in Table 1. These values of supported disappearance half-lives generally fall in the scale of years and increase with increasing chain length (Figure 6). This observation of half-life increasing with chain length is consistent with the observation that the ratio of subsurface- to surface-soil PFAs generally decreases with increasing chain length (Figure 4), possibly reflecting a stronger sorption affinity for soil of the long-chained homologues than the short-chains or a similar phenomenon.

The absence of unsaturated fluorotelomer acids in any sample (Tables SI9 and SI10) is noteworthy given their role as intermediates in the degradation of *n*-FTOHs to *sec*-FTOHs (13), both of which were in most sludge-applied surface-soil samples of our study (8). Assuming the unsaturated fluorotelomer acids are intermediates in the sludge-applied soils of this study, these nondetections suggest their disappearance half-lives are less than those we calculate for the perfluorocarboxylic acids (Table 1) or the FTOHs (8). Estimating the upper limit on half-lives of these acids using our detection limits (Table SI10), and eq 1 and the surface-soil 8:2*n*FTOH data of our accompanying paper (8), we estimate the disappearance half-life for the 8:2 unsaturated acid is <0.3 yr and the 10:2 unsaturated acid is <0.2 yr.

Estimated Unsupported Disappearance Half-Lives. Because supported PFA-fate properties evidently include the effect of ongoing ingrowth from degradation of *s*-FTOHs (Figure 5), these values (Table 1) likely overstate the persistence of these compounds when they are present in soil without any precursors. The persistence in soil of these compounds, in the absence of precursors, can be estimated according to the following (see SI for derivation):

$$[PFA] = \frac{k_{sFTOH}^u [sFTOH] (1 - e^{-k_{PFA}^u t})}{k_{PFA}^u} + [PFA]_0 e^{-k_{PFA}^u t} \quad (3)$$

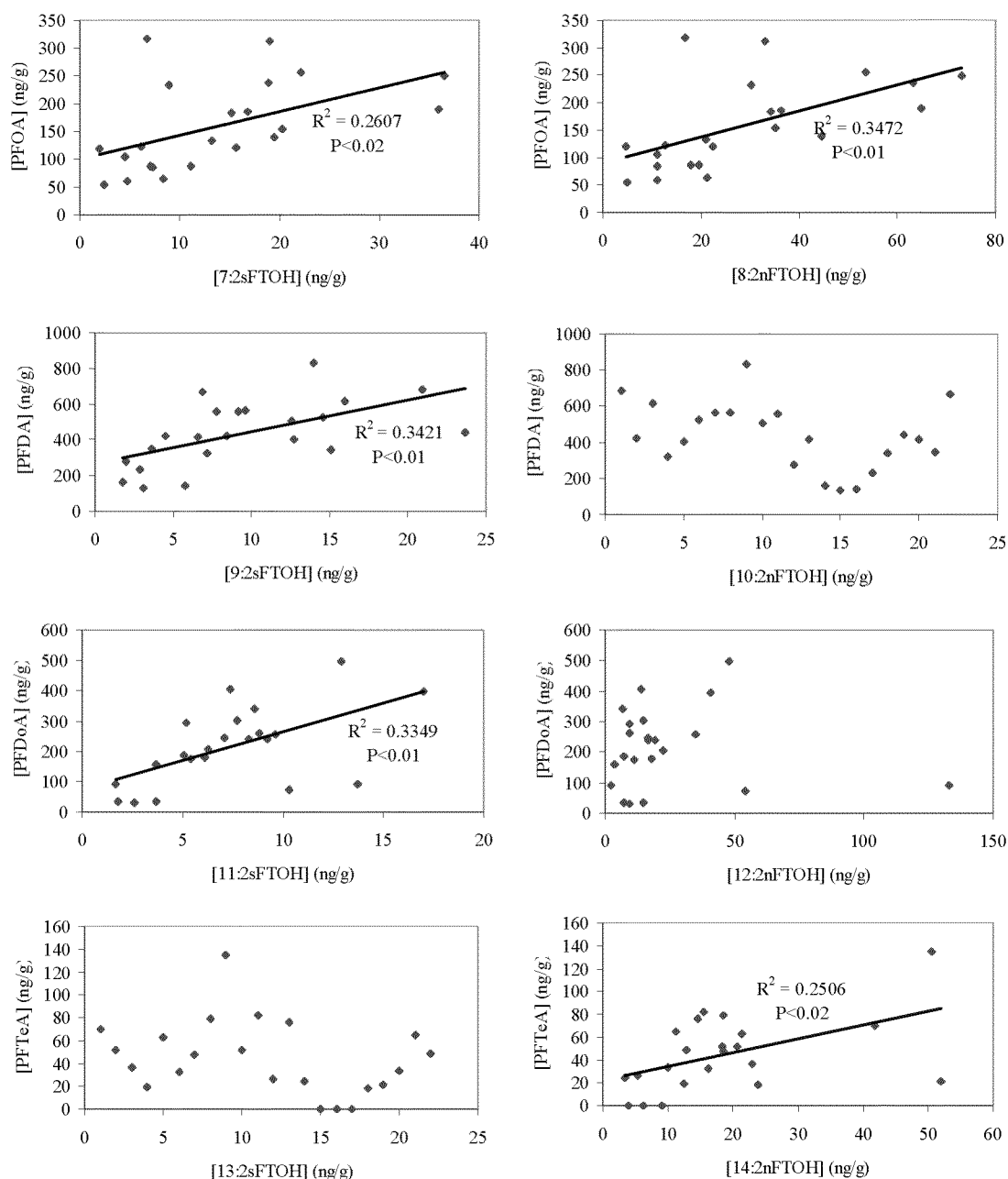


FIGURE 5. PFCAs in surface-soil samples ($n = 23$) as a function of FTOH precursors (ng/g dry soil). Acids generally are more strongly correlated with the *sec*-FTOHs than the *n*-FTOHs, presumably at least partly because the *s*-FTOHs are immediate precursors whereas the *n*-FTOHs are more remote precursors.

where k_{sFTOH}^u and k_{PFA}^u are the unsupported degradation constants of the PFA's precursor *sec*-FTOH and PFA, respectively. Equation 3 can be used to estimate the unsupported degradation constants of PFAs, given knowledge of the concentrations and unsupported degradation constant for the *s*-FTOH as reported in our accompanying paper (8), by taking the maximum [PFA] measured at 1.2 yr (Table S11) to approximate $[\text{PFA}]_0$, and by minimizing the sums of squared errors between the estimated and observed values of [PFA]s as a function of k_{PFA}^u estimates. Estimates of unsupported degradation constants and half-lives are provided for PFOA and PFDA in Table 1. The estimated unsupported half-life for PFOA is 90% of the supported, and the unsupported half-life of PFDA is only 70% of its supported value.

Values derived from eq 3 are only as good as those of the input independent values. The values we used for unsup-

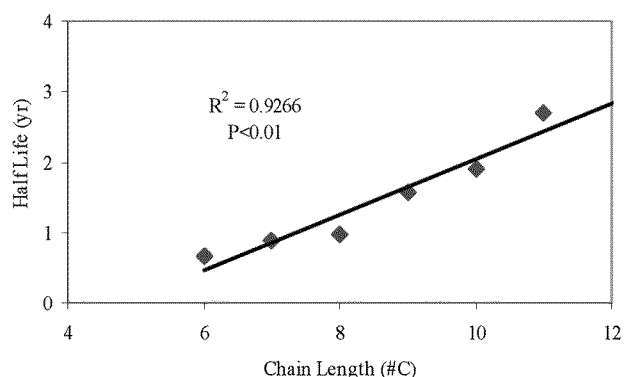


FIGURE 6. Calculated supported disappearance half-lives as a function of chain length ($n = 5$).

ported k_{sFTOH}^u were estimated from the concentrations of the s-FTOHs, their *n*-FTOH precursors, and calculated disappearance constants for the *n*-FTOHs (8). To the extent that the *n*-FTOHs were supported by precursor compounds, the resulting values for k_{sFTOH}^u and k_{PFA}^u might be underestimated. In turn, the corresponding values for $T_{1/2}^u$ might be overestimates. We have no data on the presence or absence of *n*-FTOH precursor compounds, but polyfluoroalkylphosphoric acids (PAPs) (16) and fluorotelomer-based polymers (11) both are potential sludge constituents that have been shown to degrade to *n*-FTOHs. Considering all of this, our estimates of unsupported disappearance half-lives for PFAs in soils might best be considered upper-limiting values.

Perspective. In the sludge-applied surface soils we studied, PFA analytes summed to as high as $\sim 5 \mu\text{g/g}$ and short-chain concentrations generally fell with increasing time since last sludge application. At least part of this decrease is from leaching losses to deeper soil. This loss evidently is offset by degradation of precursor compounds to form these analytes. Modeling the net losses of these PFA analytes from the surface soil as an analyte-first-order process, we get half-lives ranging from 1 to 3 years depending on chain length. These rough field-disappearance half-life estimates contribute to development of a useful perspective for environmental persistence of these compounds when cleanup and other options are being considered.

The relevance of the soil [PFA] data we report here to the general practice of application of sludge to land is unclear because much of the sludge that was applied to the fields in this study had substantially higher concentrations of PFOA, and likely other PFAs, than other sludges that have been reported in peer-reviewed literature (Figure S11 and accompanying discussion).

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Supporting Information Available

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Supporting Information for:

Characterizing Fluorotelomer & Polyfluoroalkylate Substances in New & Aged Fluorotelomer-Based Polymers for Degradation Studies with GC/MS & LC/MS/MS

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Equation S3

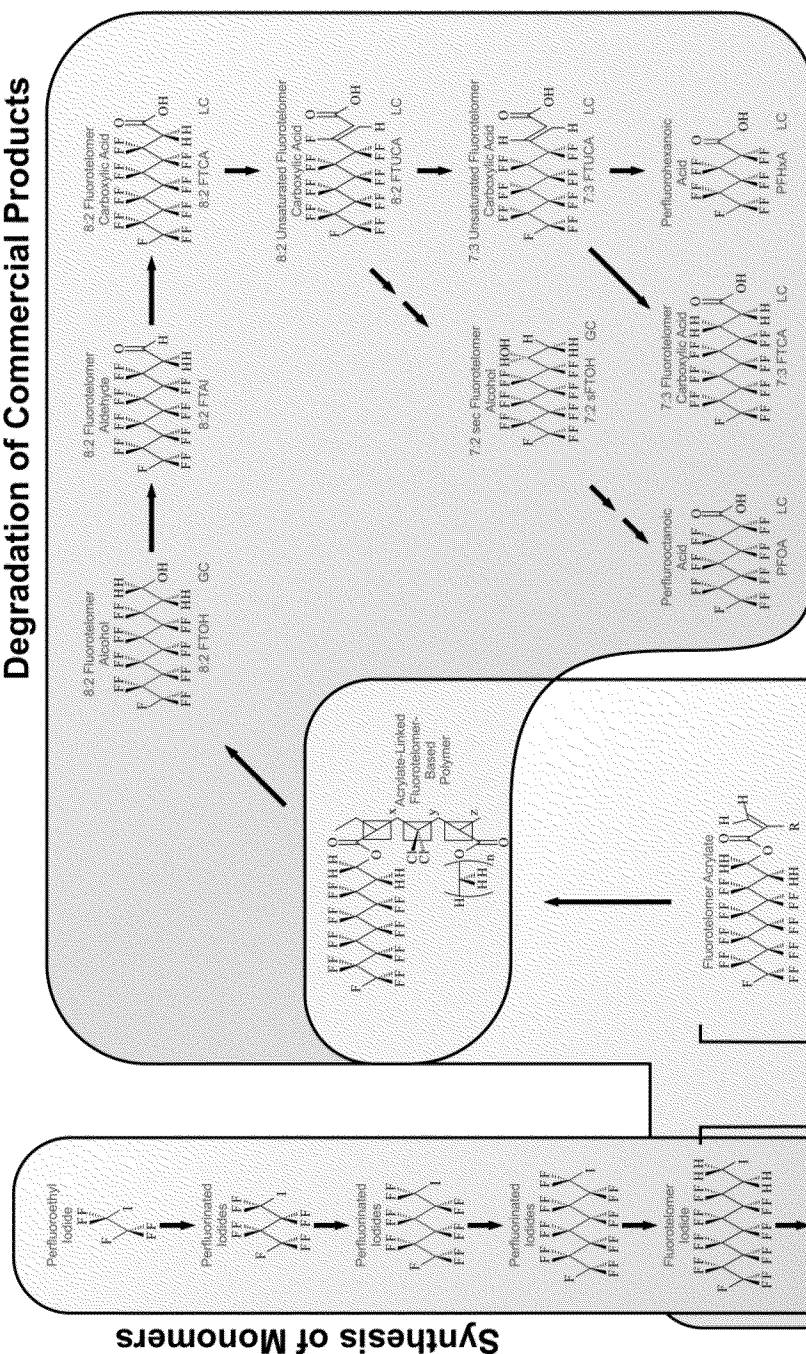
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Disclaimer

Literature cited in Supporting Information

Degradation of Commercial Products



Synthesis of Commercial Products

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Table S1: Residuals & impurities in selected FTPs & FTP sols

Residual & Impurity Chemical Species	Molecular Weight	Fluorotelomer Colloidal Solutions			Dried Fluorotelomer Polymers	
		Russell et al. 2008 Sol	Fluorotelomer Polymer Sol 3	Fluorotelomer Polymer Sol 4	Washington et al. 2009	Fluorotelomer Polymer 4
		(ug/g solid)	(ug/g solid)	(ug/g solid)	(ug/g solid)	(ug/g solid)
Residuals						
Fluorotelomer Acrylate; F(CF2)n(CH2)2OC(O)CH=CH2; n-2FTAc						
6-2FTAc	418	15	ND	ND	8.4	ND
8-2FTAc	518	4231	426	1777	117	101
10-2FTAc	618	1692	501	2057	36	65
12-2FTAc	718	NR	121	ND	<14	35
Fluorotelomer Alcohol; F(CF2)n(CH2)2OH; n-2FTOH						
6-2FTOH	364	96	108	1150	9.8	ND
8-2FTOH	464	4615	1654	31152	265	90
10-2FTOH	564	2500	845	22309	125	163
12-2FTOH	664	NR	102	4042	48	248
Fluorotelomer Iodide; F(CF2)n(CH2)2I; n-2FTI						
6-2FTI	474	<19	ND	ND	ND	ND
8-2FTI	574	<19	ND	ND	ND	ND
10-2FTI	674	<19	ND	ND	ND	ND
Perfluoro Iodide; F(CF2)nI; nPI						
6PI	546	<19	ND	ND	ND	ND
8PI	646	<19	ND	ND	ND	ND
Impurities						
F(CF2)8(CH2)2-O-C(O)(CF2)7F	860	<19	ND	ND	ND	ND
Fluorotelomer Acetates; F(CF2)n(CH2)2-O-C(O)CH3; n-2FTAt						
6-2FTAt	406	35				
8-2FTAt	506	4231	259	1571	ND	ND
10-2FTAt	606	2331	107	630	ND	ND
12-2FTAt	706	NR	ND	ND	ND	ND
Ethers; F(CF2)n(CH2)2-O-(CH2)2(CF2)mF; n-mEther						
6-8Ether	810	<38	ND	ND	ND	ND
8-8Ether	910	2308	171	390	ND	263
8-10Ether	1010	1538	55	ND	ND	202
Fluorotelomer Olefins; F(CF2)nCH=CH2; n-2FTO						
8-2FTO	446	1154	ND	ND	ND	ND
10-2FTO	546	1538	ND	ND	ND	ND
Perfluorocarboxylates; F(CF2)(n-1)C(O)OH; Cn						
C6	314	NR	3	9	0.13	7
C7	364	NR	9	17	0.077	11
C8	414	38	21	37	0.59	31
C9	464	18	46	42	0.097	4
C10	514	23	8	14	0.37	7
C11	564	9	10	9	0.047	2
C12	614	NR	2	2	0.36	3
Ratio Perfluorocarboxylates/Fluorotelomer Alcohols; Cn/(n-2)FTOH						
C6/6-2FTOH			0.0324	0.0079	0.013	
C8/8-2FTOH		0.008	0.0128	0.0012	0.002	0.338
C10/10-2FTOH		0.009	0.0099	0.0006	0.003	0.043
C12/12-2FTOH			0.0197	0.0005	0.008	0.011

ND = not detected

NR = not reported

Dried FTP4 extracted in presence of soil by method reported in this paper

Chemicals Used.

Chemicals used in this study were of the highest purity offered by the suppliers, uniformly $\geq 97\%$ purity. Unlabeled and labeled perfluorocarboxylic acids, telomer acids, telomer alcohols, telomer acrylates and all other perfluoro and polyfluoro alkylate substances were purchased as certified standards from Wellington Laboratories through TerraChem (Shawnee Mission, KS, USA). Tetrabutylammonium hydrogen sulfate (TBAHS) and sodium carbonate, were purchased from Aldrich Chemical (Milwaukee, WI, USA). Acetonitrile (ACN), glacial acetic acid, methanol (MeOH) and methyl tert-butyl ether (MTBE) were purchased from Fisher Chemical (Fairlawn, NJ, USA). Oasis HLB solid-phase extraction (SPE) cartridges, 35-cm³ capacity, were purchased from Waters (Milford, MA, USA). For the ion-pairing agent, a TBAHS mixture (TBA-mix) was prepared by slowly combining two parts 0.25 M Na₂CO₃ solution and one part 0.50 M TBAHS solution by volume to avoid spillage caused by CO₂ evolution. The resulting mixture was polished by passage through HLB cartridge to remove PFOA, which we observed to be present in the TBAHS product as purchased.

Table S2: GC/MS analytical parameters

Compound	Function Count	Calibration Standard	Apex Retention Time	PCI Mode m/z Values		
			(min)	Quantitation	Qualification	TMSI
Group 1: 5.8 to 9.5 min, 100 msec dwell, 1.11 cycles/sec						
5:2sFTOH	1	ND	?	315		
m6:2nFTOH	2	Intern Stan	7.85	369		
6:2nFTOH	3	6:2nFTOH	7.85	365	327	437
7:2sFTOH	4	7:2sFTOH	8.04	415	377	487
m8:2nFTOH	5	NA	9.15	469	431	
8:2nFTOH	6	8:2nFTOH	9.15	465	427	537
6:2FTAc	8	ND	~9.4	419		
8:2FTAAt	7	8:2FTAAt	9.42	507		
9:2sFTOH	9	ND	?	515	477	587
Group 2: 9.5 to 11.0 min, 100 msec dwell, 0.91 cycles/sec						
9:2sFTOH	1	ND	?	515		
10:2FTO	2	ND	?	547		
10:1nFTOH	3	NA	9.68	551		
11:2sFTOH	4	ND	?	615	577	687
m10:2nFTOH	5	NA	10.07	569	531	
10:2nFTOH	6	10:2nFTOH	10.07	565	527	637
8:2FTAc	7	8:2FTAc	10.19	519		
10:2FTAAt	8	10:2FTAAt	10.32	607		
12:2nFTOH	9	10:2nFTOH	10.84	665	627	737
13:2sFTOH	10	ND	?	715	677	787
10:2FTAc	11	10:2FTAc	10.96	619		
Group 3: 11.0 min +, 100 msec dwell, 1.0 cycles/sec						
13:2sFTOH	1	ND	?	715	677	787
8-8Ether	2	10:2nFTOH	11.39	911		
14:2nFTOH	3	10:2nFTOH	11.44	765	727	837
12:2FTAc	4	10:2FTAc	11.60	719		
8-10Ether	5	10:2nFTOH	11.94	1011		
16:2nFTOH	6	10:2nFTOH	12.10	865	827	
14:2FTAc	7	10:2FTAc	12.20	819		
18:2nFTOH	8	10:2nFTOH	12.60	965	927	
16:2FTAc	9	ND	12.70	919		
18:2FTAc	10	ND	~13.2	1019		

1) Chemical Abbreviations: as defined in Table S1

2) Qualification & TMSI peaks used in initial identification

3) TMSI: trimethylsilyl derivative m/z value

4) NA: not applicable to this study; ND not detected

Table S3: LC/MS/MS analytical parameters

Analyte (qn=quantification ql=qualification)	Column 43 Elution Times			Mass & Transition Parameters				Standards		Meth: C6 7 & FTCAs		Meth: C5-8-10	
	Apex	Front	Tail	Parent m/z	Fragment m/z	Cone Potential	Collision Energy	Calibration	Matrix Internal	Delta Time	Function Interval	Delta Time	Function Interval
	(min)	(min)	(min)	(D/esu)	(D/esu)	(V)	(eV)			(min)	(min)	(min)	(min)
C2 qn	0.67	0.49	0.94	113.00	69.00	13	10	C4	M3C4			0.67	0.00
C3 qn	0.77	0.52	0.91	162.80	118.80	14	11					0.10	
C4 qn	0.77	0.59	1.01	212.85	168.80	13	10					0.00	
M3C4 qn	0.77	0.59	1.01	215.95	171.90	14	10					0.00	
M3C5 qn	1.20	1.09	1.35	265.80	221.90	13	10	C5	M3C5			0.43	
C5 qn	1.20	1.09	1.35	262.80	218.85	13	10					0.00	1.40
C6 ql	1.62	1.38	1.93	312.80	118.80	13	20	C6	M2C6	1.62			
C6 qn	1.62	1.38	1.93	312.80	268.85	13	10						
M2C6 qn	1.62	1.38	1.93	314.95	270.00	14	10	C7	M2C6	0.00			
C7 qn	2.13	1.86	2.41	362.70	318.80	13	10						
C7 ql	2.13	1.86	2.41	362.70	168.85	13	18	C8	M4C8	0.51	2.85		
C8 qn	2.30	2.00	2.50	412.70	368.75	14	10						
C8 ql	2.30	2.00	2.50	412.70	168.85	14	18						
M4C8 qn	2.30	2.00	2.50	417.00	372.00	14	10						
M8C8 qn	2.30	2.00	2.50	420.95	376.00	14	11	M8C8	M4C8	0.00		0.00	2.55
5-3FTCA qn	2.61	2.52	2.70	341.00	237.00	17	12	6-2FTUCA	M2 6-2FTUCA	0.48	1.80		
6-2FTCA qn	2.74	2.63	2.83	377.00	293.00	16	17	6-2FTUCA	M2 6-2FTUCA	0.13			
6-2FTUCA ql	2.78	2.63	2.90	357.00	242.70	16	40			0.04			
6-2FTUCA qn	2.78	2.63	2.90	357.00	293.00	16	17	6-2FTUCA	M2 6-2FTUCA	0.00			
M2 6-2FTUCA qn	2.78	2.63	2.90	359.00	294.00	16	17			0.00			
5-3FTUCA qn	2.79	2.68	2.93	339.00	269.00	16	18	6-2FTUCA	M2 6-2FTUCA	0.01	3.75		
C9 ql	2.80	2.50	3.16	462.70	218.85	15	11	C9	M5C9			0.50	
C9 qn	2.80	2.50	3.16	462.70	418.70	15	11					0.00	
M5C9 qn	2.80	2.50	3.16	468.10	423.00	15	12					0.00	3.20
7-3FTCA qn	3.71	3.62	3.80	441.10	337.10	17	12	8-2FTUCA	M2 8-2FTUCA	0.92	2.90		
8-2FTCA qn	3.84	3.73	3.93	477.00	393.00	16	17	8-2FTUCA	M2 8-2FTUCA	0.13			
8-2FTUCA ql	3.88	3.73	4.00	457.00	342.70	16	40			0.04			
8-2FTUCA qn	3.88	3.73	4.00	457.00	393.00	16	18	8-2FTUCA	M2 8-2FTUCA	0.00			
M2 8-2FTUCA qn	3.88	3.73	4.00	459.00	394.00	16	18			0.00			
7-3FTUCA qn	3.89	3.78	4.03	439.00	369.00	16	17	8-2FTUCA	M2 8-2FTUCA	0.01	4.75		
C10 ql	3.20	2.70	3.50	512.90	218.85	15	20	C10	M2C10			0.40	
C10 qn	3.20	2.70	3.50	512.90	468.70	15	11					0.00	
M2C10 qn	3.20	2.70	3.50	514.90	470.00	15	12					0.00	3.60
9-3FTCA qn	4.50	4.38	4.58	541.00	437.00	16	17	10-2FTUCA	M2 10-2FTUCA	0.61	3.80		
10-2FTCA qn	4.73	4.48	4.84	577.00	493.00	16	17	10-2FTUCA	M2 10-2FTUCA	0.23			
9-3FTUCA qn	4.74	4.63	4.85	539.00	469.00	16	17	10-2FTUCA	M2 10-2FTUCA	0.01			
10-2FTUCA ql	4.88	4.75	5.00	557.00	443.00	16	38			0.14			
10-2FTUCA qn	4.88	4.75	5.00	557.00	493.00	16	17	10-2FTUCA	M2 10-2FTUCA	0.00			
M2 10-2FTUCA qn	4.88	4.75	5.00	559.00	494.00	16	17			0.00	5.55		
C11 qn	3.90	3.50	4.20	562.70	518.70	15	12	C11	M2C11			0.70	
M2C11 qn	3.90	3.50	4.20	564.90	520.00	15	13					0.00	4.30
11-3FTCA qn	5.13	5.02	5.22	641.00	537.00	17	12	10-2FTUCA	M2 10-2FTUCA	0.25	4.80		
12-2FTCA qn	5.42	5.32	5.52	677.00	593.00	16	17	10-2FTUCA	M2 10-2FTUCA	0.29			
11-3FTUCA qn	5.42	5.32	5.52	639.00	569.00	16	17	10-2FTUCA	M2 10-2FTUCA	0.00			
12-2FTUCA ql	5.71	5.52	5.78	657.00	543.00	16	38			0.29			
12-2FTUCA qn	5.71	5.52	5.78	657.00	593.00	16	17	10-2FTUCA	M2 10-2FTUCA	0.00	6.60		
13-3FTCA qn	5.83	5.72	5.92	741.00	637.00	17	12	10-2FTUCA	M2 10-2FTUCA	0.12	5.60		
14-2FTCA qn	6.12	6.02	6.22	777.00	693.00	16	17	10-2FTUCA	M2 10-2FTUCA	0.29			
13-3FTUCA qn	6.12	6.02	6.22	739.00	669.00	16	17	10-2FTUCA	M2 10-2FTUCA	0.00			
14-2FTUCA qn	6.41	6.22	6.48	757.00	693.00	16	17	10-2FTUCA	M2 10-2FTUCA	0.29	15.00		
C12 qn	4.10	3.70	4.40	612.70	568.70	16	13	C12	M2C12			0.20	
M2C12 qn	4.10	3.70	4.40	614.90	570.00	15	12					0.00	
C13 qn	4.70	4.20	4.90	662.75	618.70	16	13	C13	M2C12			0.60	
C13 ql	4.70	4.20	4.90	662.75	318.70	16	22					0.00	
C14 qn	5.60	5.00	5.90	712.75	668.70	18	14	C14	M2C12			0.90	
C14 ql	5.60	5.00	5.90	712.75	318.70	18	24					0.00	6.00
15-3FTCA qn	6.53	6.42	6.62	841.00	737.00	17	12	10-2FTUCA	M2 10-2FTUCA	0.12	5.90		
16-2FTCA qn	6.82	6.72	6.92	877.00	793.00	16	17	10-2FTUCA	M2 10-2FTUCA	0.29			
15-3FTUCA qn	6.82	6.72	6.92	839.00	769.00	16	17	10-2FTUCA	M2 10-2FTUCA	0.00			
16-2FTUCA qn	7.11	6.92	7.18	857.00	793.00	16	17	10-2FTUCA	M2 10-2FTUCA	0.29	15.00		
17-3FTCA qn	7.23	7.12	7.32	941.00	837.00	17	12	10-2FTUCA	M2 10-2FTUCA	0.12	6.10		
18-2FTCA qn	7.52	7.42	7.62	977.00	893.00	16	17	10-2FTUCA	M2 10-2FTUCA	0.29			
17-3FTUCA qn	7.52	7.42	7.62	939.00	869.00	16	17	10-2FTUCA	M2 10-2FTUCA	0.00			
18-2FTUCA qn	7.81	7.62	7.88	957.00	893.00	16	17	10-2FTUCA	M2 10-2FTUCA	0.29	15.00		
C15 qn	6.30	5.70	6.6	762.75	718.70	16	13	C14	M2C12			0.70	4.3
C16 qn	7.00	6.40	7.3	812.70	768.70	16	13	C14	M2C12			0.70	
C17 qn	7.70	7.10	8	863.00	819.00	15	12	C14	M2C12			0.70	
C18 qn	8.40	7.80	8.7	912.75	868.70	18	14	C14	M2C12			0.70	15

Discussion S1: Typical Analytical Difficulties with FTPs & FTP Sols.

Discussion S1.1 Variation of Detected Residuals with Choice of Solvent & FTP sol. A central operational objective in characterizing residuals in FTP sols is to open the FTP structure, thereby bolstering dispersion of the FTP particles and fluorotelomer monomers in the bulk solvent⁴. If the interfacial free energy between the FTP and the liquid phase is too high, the FTP will not dissolve, an outcome common for numerous solvents (Figure S2). Given the mutual affinity of FTSs for each other, those solvents that do not dissolve FTPs effectively, likewise, tend to dissolve FTS monomers only sparingly from FTP substrates into the bulk liquid, with the FTS monomers instead remaining closely associated with undissolved FTP particles. Further, whereas the capacity of a solvent to disperse FTP particles is requisite for characterizing FTS residuals, this criterion alone is not sufficient to assure an accurate assessment of FTS content in an FTP. To the extent FTS monomers remain associated with dispersed FTP particles, whether sorbed or as a diffuse layer surrounding the FTP, instead of dissolving homogeneously into the bulk solvent, this monomer fraction can remain unaccounted for with analysis, e.g., in chromatographic analysis, FTP-sorbed FTSs are not free to elute at their characteristic retention times. For example, Figure S3 summarizes concentrations of two fluorotelomer alcohols for two FTP sols that have been dissolved in THF and MTBE; starting with identical aliquots of FTPs added to identical solvent volumes, MTBE returns less FTP than THF for FTP3, but more for FTP4, and the discrepancy between solvents is larger for 8-2FTOH than 10-2FTOH for both polymers.

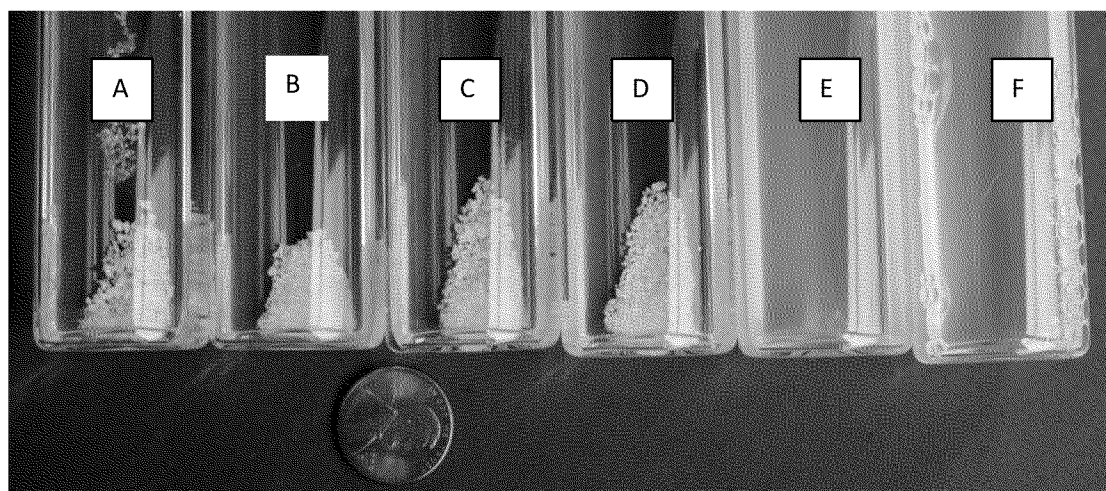


Figure S2: Photo of an FTP in selected solvents from Washington et al.⁵ with permission of the authors. A test acrylate-linked fluorotelomer-based polymer (AFTP) in candidate extraction solvents. The persistence of granular AFTP in water (S2a), methanol (MeOH; S2b), 60% acetonitrile/40% water (ACN/H₂O; S2c) and 93% ACN/7% 200 mM NaOH (S2d) indicates that the surface tension of the liquids exceeds that of the AFTP phase so that the solid particles are stable. In contrast, methyl tert-butyl ether (MTBE; S2e) and tetrahydrofuran (THF; S2f) have sufficiently low surface tensions to ‘dissolve’ the solid AFTP. Solvents in which the solid AFTP is stable cannot wet the AFTP⁶, leaving AFTP particle interiors and associated perfluorinated

molecules effectively shielded from solvent extractions. The ACN/NaOH solvent shown above, with the solid AFTP particles remaining undissolved (S2d), is the same solvent used by Russell *et al.*⁷ to extract their soil/AFTP microcosms. The MTBE (S2e) and ACN/H₂O (S2c) were the primary and secondary solvents used in our extraction albeit at lower [ACN] than our final method. The appearance of the MTBE, apparently clouded by AFTP micelles, compares closely with that of the THF (S2f) which Larsen *et al.*⁴ identified as effective for extracting fluorotelomer chemicals.

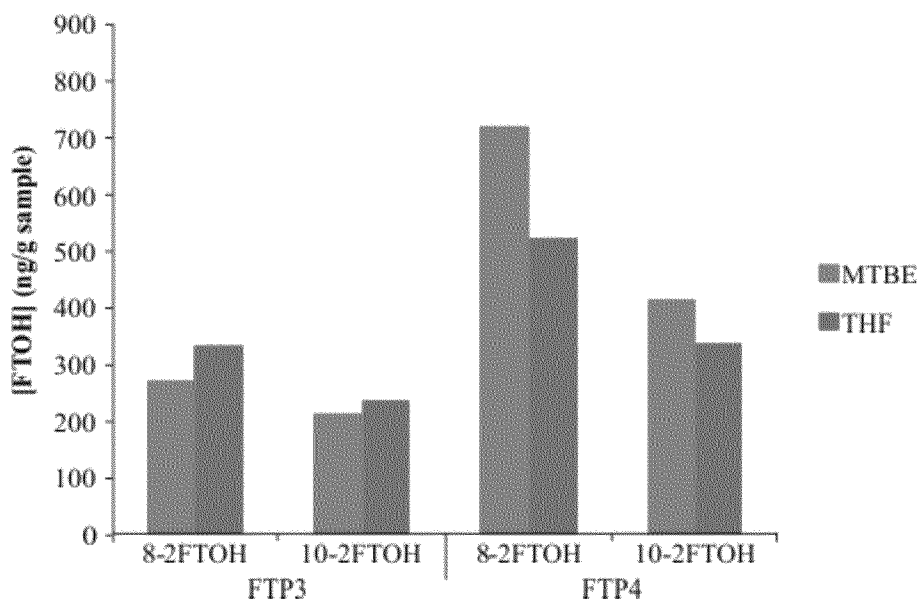


Figure S3: FTOHs in FTP3 & FTP4 sols dissolved in MTBE & THF. MTBE returns lower concentrations of both analytes than THF for FTP3, but higher values for FTP4. A common phenomenon for FTP sols in our experience, we suspect that fluorotelomer monomers are not homogeneously dissolved from the FTP sols into bulk solvents, with fractions remaining closely associated with, or diffusely sorbed to, the suspended FTP particles, similar to the FTP aggregation observed in THF and chloroform by Rankin and Mabury⁸.

Discussion S1.2 FTP sols can contaminate analytical systems. Given the dual functionality of FTPs, having non-fluorinated anchoring groups and fluorinated omni-phobic chains, variable pressures and temperatures encountered during GC/MS analysis can cause the FTP to plate out on instrument surfaces that vary between FTPs, e.g., inlet surface vs MS source surface. For the FTP of our first study⁵, extracts of our acrylate-linked FTP posed few analytical complications. In contrast, in a cooperative research effort between the EPA and DuPont, a GC/MS was contaminated by injection of urethane-linked FTP-sol samples during method development⁹;

blanks injected prior to the polymer samples returned baseline signal as expected, but following injection of the FTP sample, blanks returned quantifiable peaks for several fluorotelomer monomers, and the signals for standards increased post-FTP samples as well. These results were interpreted as ‘carryover,’ suggesting that some of the FTP plated out in the GC inlet with desorption of fluorotelomer monomers from the plated FTP or thermal degradation of the FTP with subsequent injections.

In efforts with an acrylate-linked FTP sol, this one containing poly-ether nonfluorinated groups, we did not experience contamination of blanks, which indicated plating out of the FTP in the GC inlet as argued above, but we did encounter decreasing signal strength with each sample injection (Figure S4). With cleaning of the fouled MS ion source, the MS signal returned to its initial sensitivity (Figure S4). We interpreted this pattern as suggesting that the FTP did not plate out in the GC inlet, but did effectively ‘paint’ the MS ion surface, progressively decreasing its efficacy for ionizing samples with each sample injection. These results with plating out in the GC inlet and on the MS ion source, contrasted with our experience with acrylate-linked FTP4, for which we encountered no problems (Figure S4).

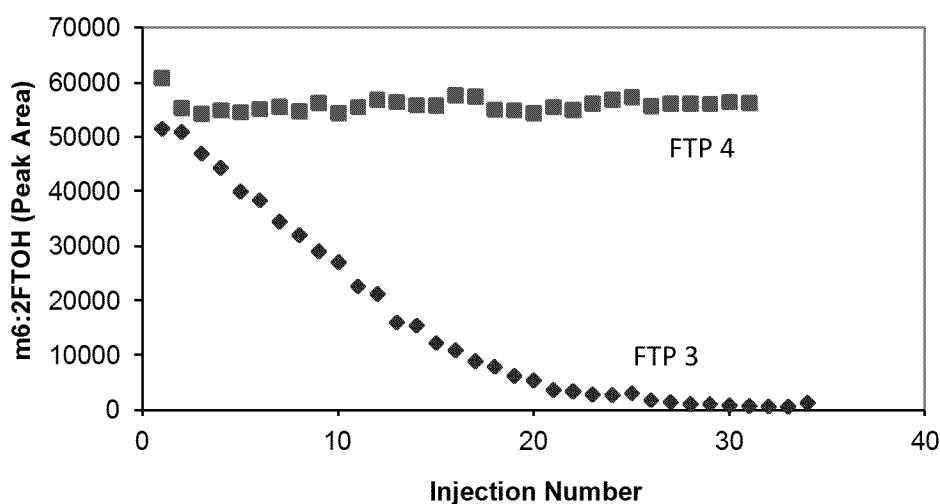


Figure S4: Repeated GC/MS runs of FTP3 & FTP4 sols. Peak Area of mass-labeled 6:2FTOH (*m*6:2FTOH), which was added to all samples at the same concentration as a matrix internal standard, in samples containing two different FTP sols. For FTP3 sol (diamonds), signal strength decreased with each sample injection. For FTP4 sol (squares), signal strength remained roughly constant after the initial sample. Notably, use of the mass-labeled 6:2FTOH as internal standard allowed acceptable quantification for both FTPs. An injection of 125 ng/mL standard returned 135 ng/mL before FTP3 was injected and it returned 114 ng/mL after 24 injections of FTP3.

Based on these efforts, direct analysis of fluorotelomer monomers by GC/MS can be complicated for samples of some FTP sols. In these cases, employment of alternative analytical techniques, e.g., derivitization followed by LC/MS/MS analysis¹⁰, might be necessary.

Discussion S1.3 Aged FTPs can contaminate instruments after methods are developed & studies are initiated. A common objective in studies of FTPs is to determine their stability with aging, and whether they might degrade to form perfluorinated compounds of health and environmental concern. Such studies entail substantial methods development work with new FTP products. Unfortunately, methods found suitable with new FTP products are not necessarily so if the FTP is found to be unstable over the course of an aging study. Figure S5 illustrates this effect over the course of a roughly eight-month FTP-aging experiment. Having an interest in retaining a single methodology over the course of the experiment, and given that future samples can be expected to impact the analytical system similarly, cleaning the analytical system to revert to the original analytical condition might negatively impact study continuity, i.e., if peak morphology changes drastically from ideal in a newly cleaned system over the course of running samples, acceptable quantitation could be lost.

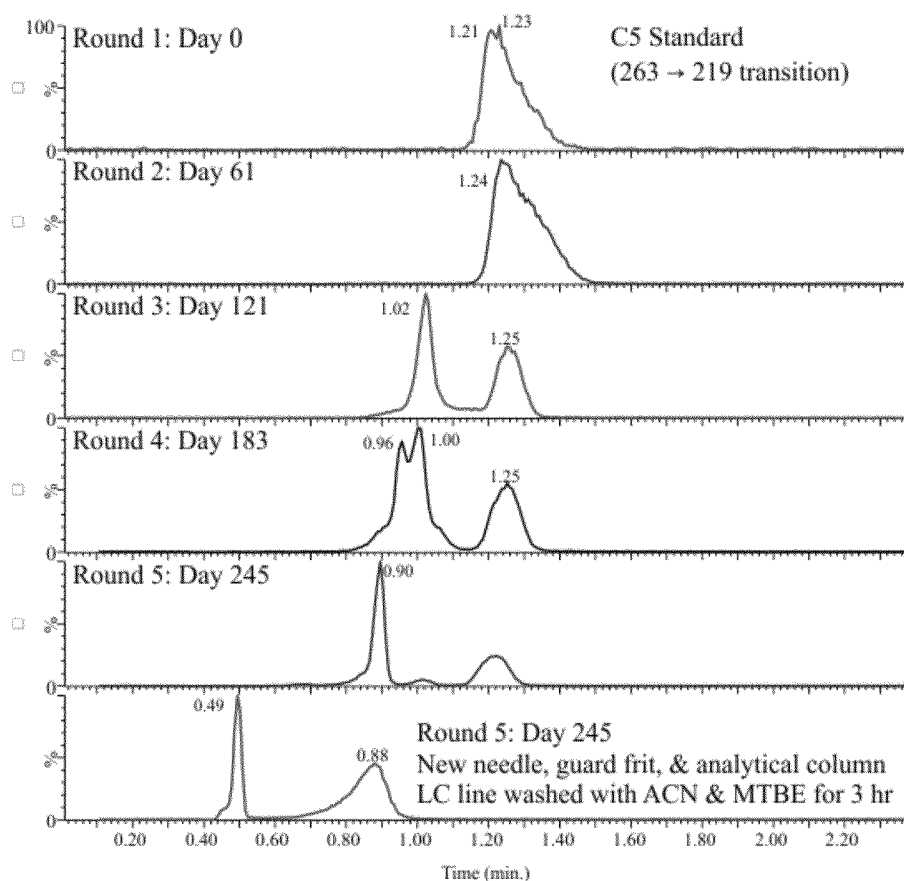


Figure S5: PFPeA (C5) standard on LC/MS/MS run bimonthly during an FTP degradation study over the course of an eight-month FTP degradation study. At initiation of the study, C5 eluted with expected mononodal peak shape. This shape was retained at 60 days, at which time little to no FTP degradation was suspected. With subsequent sampling rounds, C5 evolved into a binodal peak. Fortunately, total peak area remained roughly constant throughout this period of study. Note that the last chromatogram was collected after replacing the sampling needle, guard frit and analytical column. We suspect that degraded FTP or related degradation products coated most of the flow path from needle to MS ESI inlet and acted as an artifactual stationary phase. This effect grows less pronounced with increasing chain length; it is present as a minor fronting lobe on C8 and only as fronting asymmetry on longer chains.

Discussion S1.4 Extraneous analyte-type peaks on some FTPs. Among potential matrix complications presented by FTPs and FTP sols, when synthesis components are unknown to the analyst, some FTPs can yield extraneous peaks that meet several analyte identification criteria (Figure S6). Depending on study objectives, these extraneous peaks can manifest ambiguities: are these peaks from FTOH isomers? Might these compounds degrade to form perfluorinated compounds of ill-defined source? Are these compounds components of the FTP or only present as monomers in the FTP sol?

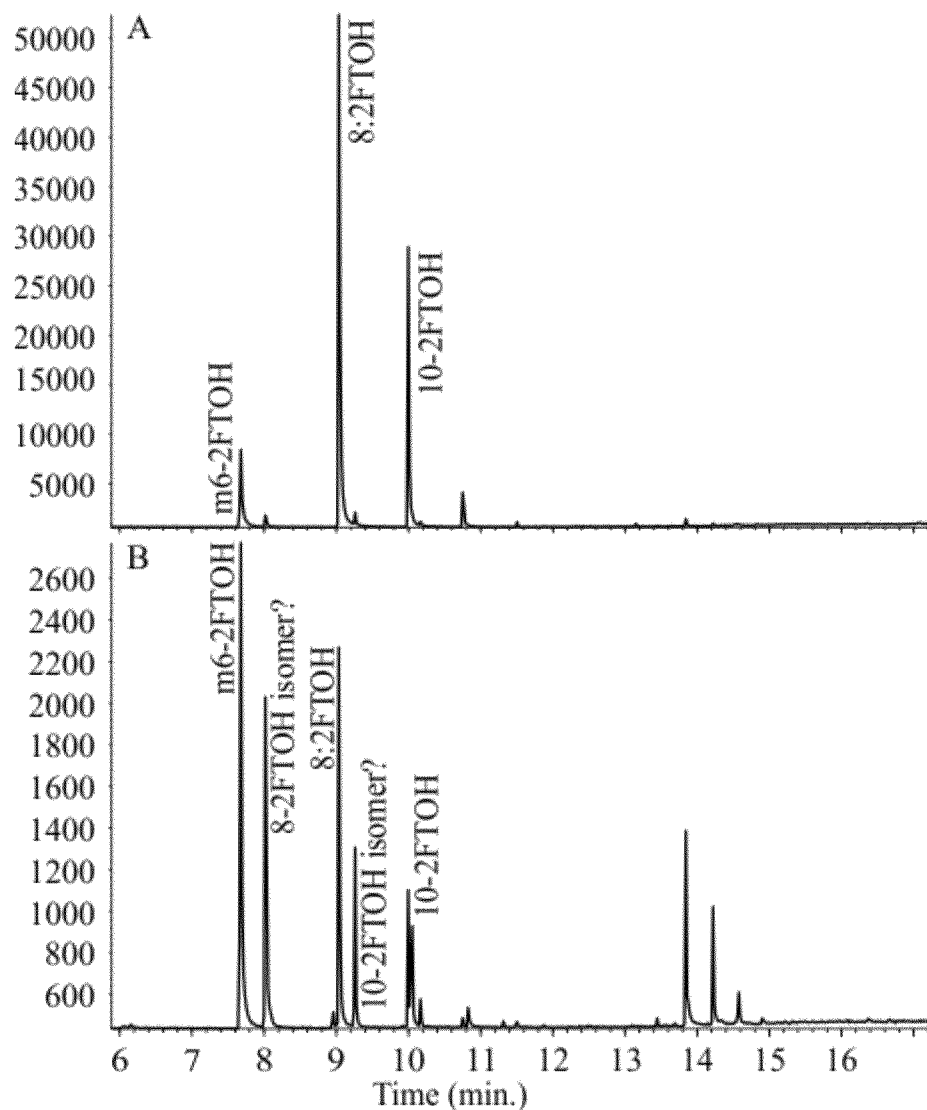


Figure S6A & B: GC/MS selected-ion chromatograms of two FTP-sols monitoring the m/z for 8-2FTOH, 10-2FTOH, 12-2FTOH and mass-labeled 6-2FTOH (added as a matrix internal standard). In the FTP of 6A, only the expected analytical peaks appear. In contrast, the FTP of 6B exhibits extraneous peaks meeting numerous identification criteria for fluorotelomer compounds (parent m/z , fragment m/z , $\Delta m/z = 100$ D/esu characteristic of $2CF_2$, similar interval in elution times between hypothetical homologues).

Discussion S2: Comparison of FTOH residuals in FTP4 prepared by selected methods to anticipated degradation products for modeled half lives

The impact of residual fluorotelomer monomers in FTPs, on detecting FTP degradation, as inferred by increasing degradation-product concentrations during FTP incubation in environmental media, can be qualitatively assessed by comparing high-concentration residual levels to the concentrations of degradation products expected over a range of possible FTP half lives. Referring to Table S1, of all the residuals in the sol of FTP4, 8-2FTOH and 10-2FTOH are present at the highest concentrations. Based on this, we will compare residual 8-2FTOH and 10-2FTOH to the modeled concentrations degradation products.

The residual values of 8-2FTOH and 10-2FTOH in FTP4 shown in Figures 2 and S7 are summarized below in Table S4.

Table S4: Residuals in FTP4 for selected preparations

FTP Condition	Residual [8-2FTOH] (umol/g solids)	Residual [8-2FTOH] (% Comm. Sol)	Estimated Max T1/2 (1) (yr)	Residual [10-2FTOH] (umol/g solids)	Residual [10-2FTOH] (% Comm. Sol)	Estimated Max T1/2 (1) (yr)
Commercial Sol (2)	160	100	1.4	78	100	1.8
Purified Raws Sol (2)	107	67	2	63	81	2.3
Dried at 21 C (3)	61	38	4.3	43	55	3.6
Dried at 50 C (3)	11	6.9	25	20	26	8.1
Dried at 127 C (3)	0.3	0.19	200	0.2	0.26	200

(1) Estimated Max T1/2 is the maximum FTP degradation half life that is expected to yield recoverable degradation products equaling or exceeding the initial residual FTOH concentration of the FTP in a one-year degradation experiment.

(2) Grab samples of sols as delivered to EPA. Commercial is commercial stock FTP sol. Purified Raws is the generally lowest-concentration sol delivered to EPA of four preparation treatments (see Figure 3 of paper)

(3) Dried from a subsample drawn from the Purified Raws stock sol after mixing on a ball mill for several hours.

To estimate the concentrations of degradation products expected as a function of FTP half lives, we assume: 1) FTP degradation proceeds at a single rate (independent of side-chain length) that is first-order dependent on FTP concentration; 2) all degradation products are known and measured so that the molar concentrations can be summed and related through a first-order rate equation to FTP side chains on a mole-for-mole basis; 3) based on the patent ¹¹, a reasonable estimate of 8-2FTAc side chains is 42% by mass of dry FTP (8×10^5 nmol/g dry FTP) and 10-2FTAc side chains is 26% by-mass of dry FTP (4×10^5 nmol/g dry FTP); 4) 8-2FTAc side chains give rise solely to 8-2 monomers, and the same for 10-2FTAc side chains, that is 10-2FTAc do not give rise to 8-2FTAc and 8-2FTAc are not lost to 6FTAc; 5) we will not achieve a higher molar recovery of 8-2 residuals and their degradation products than the highest reported recovery for 8-2FTOH degradation experiments in peer-reviewed literature, that of Liu, Wang and others

¹², 64% for 8-2FTOHs; 6) based on the recovery of Liu et al for 6-2FTOH of 56%, we estimate the highest recovery we might achieve for 10-2FTOH is $(0.64 \times 0.64 / 0.56) = 73\%$; 7) based on experimental data we plan to report in the future, a typical uncertainty for the sum of homologous analytes among 5 FTP-soil microcosms is a coefficient of variation (COV) of 10%; 8) at a qualitative level, $2 \times \text{COV}$ is a reasonable approximation of the 95% confidence interval about the mean.

For these assumptions, the first order degradation constant (k) is calculated from specified half life ($T_{1/2}$) by $k = \ln(2)/(T_{1/2})$ and for a one-year degradation experiment, the fraction of FTP remaining (FTP/FTP_0) is given by $\text{FTP}/\text{FTP}_0 = e^{(-k \times 1)} = e^{(\ln(0.5)/(T_{1/2}))}$ where the exponential number 1 represents the one-year period of the experiment. Then the 8-2 monomers are calculated according to $(8\text{-}2\text{FTOH equivalents generated}) = (8 \times 10^5 \text{ nmol/g dry FTP})(1 - \text{FTP}/\text{FTP}_0)$. Then based on the recoveries of Liu et al., $(8\text{-}2\text{FTOH equivalents recovered}) = (8\text{-}2\text{FTOH equivalents generated}) \times 0.64$. Then the approximated lower 95% is given by $(8\text{-}2\text{FTOH 95\% CI}) = (8\text{-}2\text{FTOH equivalents recovered}) \times 0.8$. Overall then:

$$(8 - 2\text{FTOH}95\% \text{CI}) = (8 \times 10^5 \text{ nmol / g dry FTP})(1 - e^{[\ln(0.5)/T_{1/2}]})(0.64)(0.8) \quad (\text{S1})$$

And for 10-2FTAc side chains:

$$(10 - 2\text{FTOH}95\% \text{CI}) = (4 \times 10^5 \text{ nmol / g dry FTP})(1 - e^{[\ln(0.5)/T_{1/2}]})(0.73)(0.8) \quad (\text{S2})$$

Equation S1 above was used to plot the degradation lines on Figure 2 and Equation S2 was used to generate the degradation values plotted below on Figure S7.

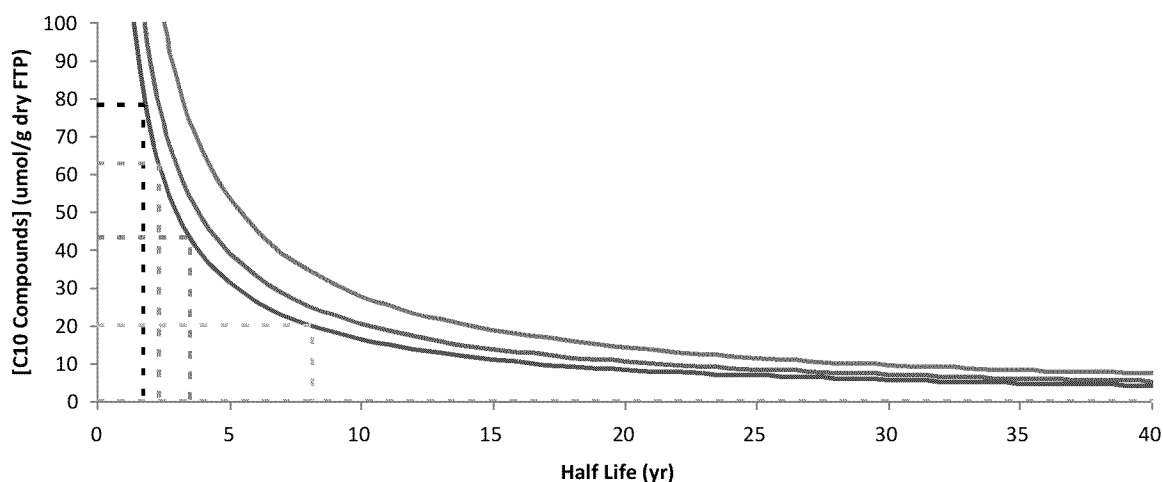


Figure S7: Residual [10-2FTOH] for selected treatments of FTP4 compared to expected FTP degradation-product concentration as a function of modeled FTP4 half life. Solid lines are modeled degradation product concentrations as a function of half life: products generated

(blue), products recovered by extraction (pink), typical 2-standard-deviation uncertainty among reps (yellow). Dashed lines are residual 10-2FTOH equivalents to half lives for: commercial sol (1.8 y), purified raws sol (2.3 y), 21 C dried (3.6 y), 50 C dried (8.1 y), and 127 C (≥ 200 y). See Discussion S2 for reasoning and justification.

Taken altogether, comparison of the modeled degradation product concentrations to the observed residual concentrations (Figures 2 & S7) can be conceived as an assessment of the experimental signal-to-noise (degradation-products-to-residuals) ratio. From this perspective, Figures 2 and S7 depict a qualitative metric of the sensitivity of the experimental design to detect FTP degradation. Given that the shortest modeled FTP half lives reported in the literature are on the order of 20 years⁵, the only FTP preparation depicted in Figures 2 and S7 that reasonably might be expected to detect FTP degradation is drying the FTP at 127 C.

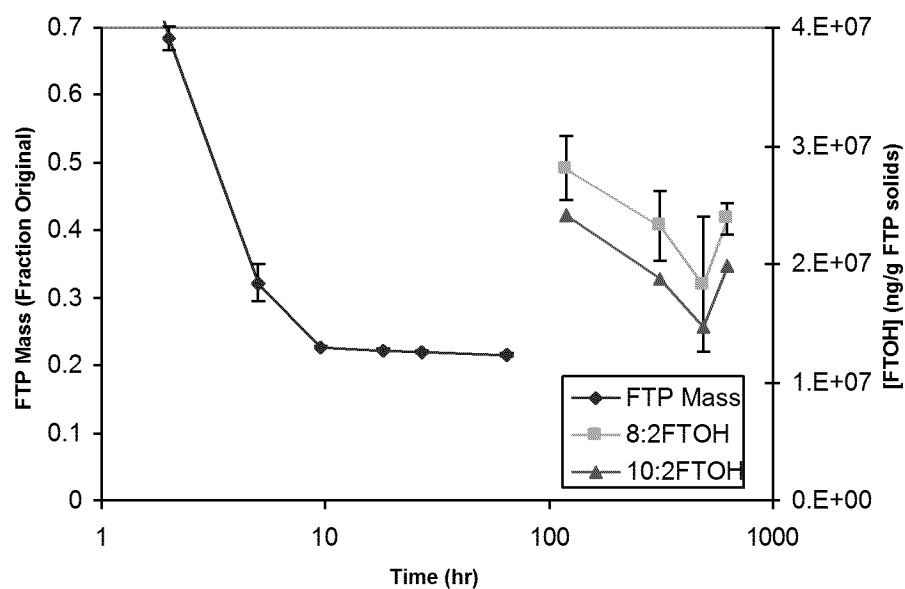


Figure S8: Mass & [FTOH] of FTP4 vs time during air drying. Error bars for replicate pairs are depicted for 8-2FTOH, but omitted for 10-2FTOH for clarity. Forgoing quantitative assessment due to small sample number, judging from the relatively high first value at 118 hr, FTOH loss seemingly can continue long after mass stabilization during air drying.

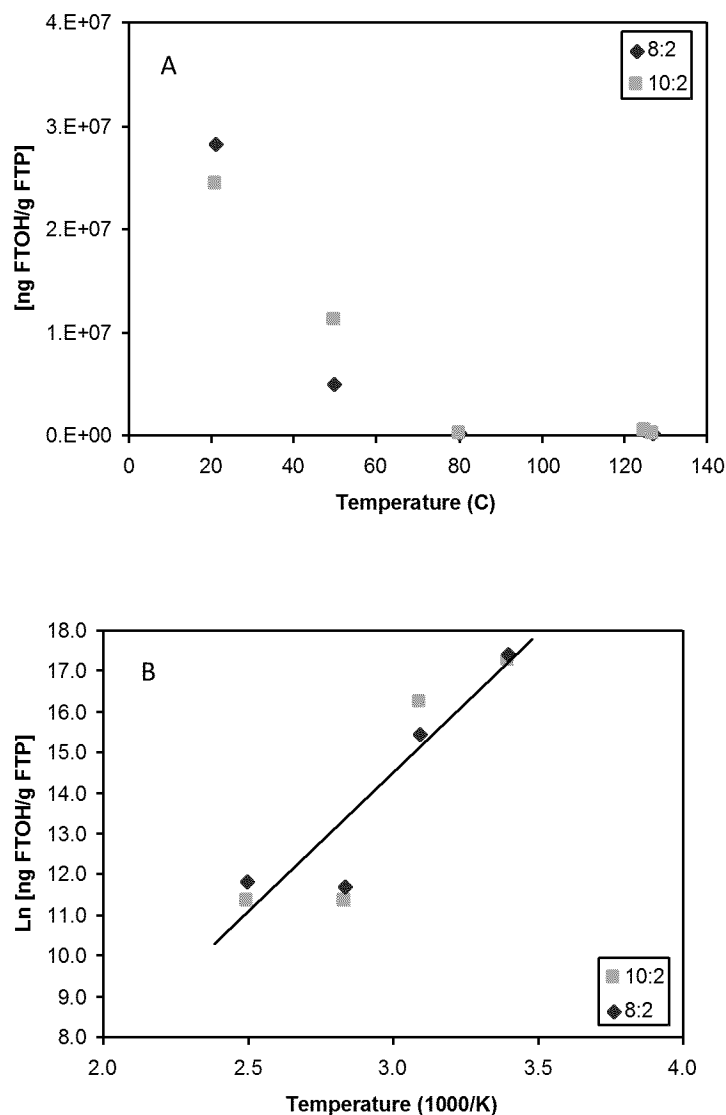


Figure S9: FTOHs in test FTP4 as a function of drying temperature exhibit a roughly 500-fold decrease at 127 C relative to the original FTP sol. Assuming the [FTOH]s in the circulating air of the oven remained roughly constant at all drying temperatures, and that volatilization proceeded until FTOHs remaining on the FTP equilibrated with this oven air, we modeled FTOHs on the FTP according to a van 't Hoff function (Figure S9b). For 8-2FTOH, the fitted van 't Hoff equation was $\ln[8:2\text{FTOH}] = 6820/T - 6.07$ where T is temperature in degrees Kelvin ($r^2 = 0.86$).



Figure S10: Configuration of oven with flow-through circulation for drying FTP sols on cotton-tuft substrate without accumulating fluorotelomer monomers in the oven headspace. Flexible copper tubing (1/4" OD) extends from the oven floor, up the back oven wall, along the oven ceiling, through the thermometer-mount portal in the oven ceiling, along the oven exterior to a water bath where the copper is coiled to cool the exhausting air. The copper tubing then extends above the water bath to join Tygon tubing which leads to house vacuum. When drying FTP samples in the oven, the vacuum is engaged, drawing lab air into the oven-top portal, where it wends its way around trays holding the FTP samples, and out through the copper draw at oven bottom. The oven temperature needs to be calibrated with the exhaust system engaged and sample trays in place.

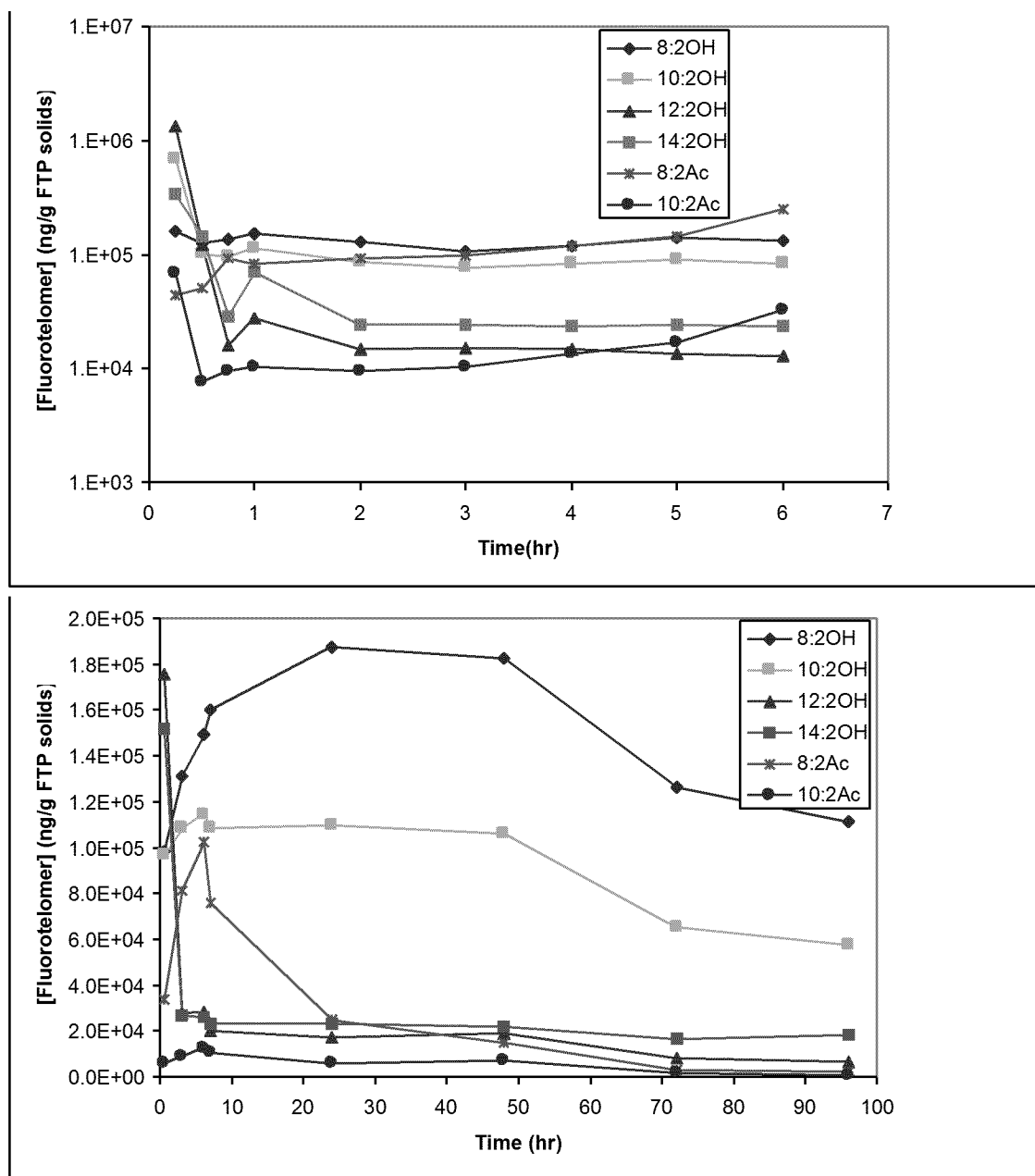


Figure S11: FTP monomer residuals as a function of protracted drying time at 127 °C. Arithmetic mean ($n=3$) for both graphs. A geometric y axis is depicted for the 6-hr run, necessitated by high concentrations for the first sample drawn at 15 minutes. An arithmetic y axis is employed for the 96-hr run, with the first sample at 30 minutes, after the precipitous initial decrease.

Discussion S3: Modeling efficacy of extraction of perfluorocarboxylate homologues as a function of free energy of sorption on a fluorotelomer stationary phase

The thermodynamic properties for the exchange of perfluorocarboxylates (PFCAs) between ACN/H₂O solutions and a fluorotelomer-based polymer phase have been reported by Marchetti et al.¹³. These investigators performed tracer pulse chromatography experiments to determine the retention properties of C5 through C8 perfluorocarboxylates on a liquid chromatographic column comprised of a perfluorohexyl stationary phase (Fluophase-RP, Thermo Scientific). Observing a retention minimum for all four perfluorocarboxylates at ACN/H₂O of 90/10, the investigators then chose three ACN/H₂O compositions, 60/40, 80/20 and 90/10, for which they determined retention of C5 through C8 at a variety of temperatures. In turn, these experimental data allowed the researchers to calculate the enthalpy and entropy of sorption to the FTP-stationary phase from the bulk ACN/H₂O solution for all four experimental perfluorocarboxylates as well as the fluoromethyl moiety, –CF₂–. From these values, Marchetti et al. calculated and reported the free energy of reaction, ΔG° , for C5-C8 and –CF₂–, for sorption to their perfluorohexyl stationary phase from 60/40, 80/20 and 90/10 ACN/H₂O.

Treating Marchetti et al.'s¹³ perfluorohexyl-sorption database as a proxy for FTPs, which admittedly generally are comprised dominantly of longer fluorotelomers, using the volumes for i) the fluorotelomer polymer in our microcosms and ii) the solvents used in our extractions, we can estimate the efficacy of our extraction method for exhausting the FTP of long chain perfluorocarboxylates. We dose our microcosms with 10 μ L of FTP4 sol. Based on numerous replicate measures, FTP4 sol has a density of 1.103 mg/ μ L and contains 19% solids by mass. Assuming the bulk aqueous phase of FTP4 sol has a density of 1.000 mg/ μ L, we can estimate the density of FTP4 solids to be 1.129 mg/mm³. From this, we can estimate the volume of FTP4 solids added to a microcosm is 0.001855 cm³ from a 10 μ L aliquot of FTP4 sol. We perform extractions with four serial volumes of 5 cm³ of ACN/H₂O.

Starting with Marchetti et al.'s ΔG° data for sorption of C5 through C8 on the FTP stationary phase from 60/40, 80/20 and 90/10 ACN/H₂O, and estimating the same for C9 through C16 using Marchetti et al.'s ΔG° data for –CF₂–, we calculate the equilibrium sorption constants (K_s) according to:

$$K_s = e^{(-\Delta G^\circ / RT)} \quad (\text{S3})$$

where ΔG° is reported in units of J/mol, R is the universal gas constant (8.314 J/(mol*K)), and T is degrees K (23 C in our laboratory, 296.15 K). The resulting value, K_s , describes equilibrium activities in the sorbed phase (mol/cm³) divided by that of the liquid phase (mol/cm³). Assuming the quotient for activity coefficients in the sorbed divided by liquid phase is unity, justified by the otherwise inherently rough nature of this estimate, K_s relates the equilibrium concentration in the sorbed to that of the liquid phase. Taking the inverse of this sorption constant, K_s , yields a

dissolution equilibrium constant, K_d , which is the equilibrium liquid concentration divided by the sorbed concentration with units of mol/cm^3 in both phases.

Multiplying an arbitrary assumed sorbed concentration, say $1 \text{ mol}/\text{cm}^3$, by K_d yields the liquid concentration that is in equilibrium with the sorbed phase. Multiplying the liquid and sorbed concentrations by their respective experimental volumes, 5 cm^3 and 0.001855 cm^3 , yields the number of moles in the liquid (M_l) and the sorbed (M_s) phases at equilibrium for our experimental extraction. From these values one can calculate the fraction of PFCA remaining sorbed to the FTP after extraction according to $M_s/(M_l+M_s)$. Since extraction proceeds according to these equilibrium constants and unchanging volumes of FTP and liquid in each extraction step, the ratio $M_s/(M_l+M_s)$ remains constant with each extraction step and the fraction remaining in the sorbed phase after n extraction step simply is $[M_s/(M_l+M_s)]^n$. And the fraction extracted at each extraction step, n , is the assumed sorbed concentration minus this value, $\{1 - [M_s/(M_l+M_s)]^n\}$.

Using this approach, we estimate the theoretical efficacy of our procedure for extracting perfluorocarboxylates from FTPs with ACN/ H_2O as reported in Figures S11A through S11C. Figure S11A strongly supports the limited efficacy we found for extracting perfluorocarboxylates from our test FTP with 60/40 ACN/ H_2O (as reported in the body of our paper). Also, Figure S11C suggests the near complete theoretical efficacy of our procedure for exhausting perfluorocarboxylates from an FTP when using the 90/10 ACN/ H_2O composition we settled on for our final method. These theoretical calculated efficacies may well overestimate the true efficacy of our procedure however because, i) commercial FTPs generally are comprised dominantly of longer-chain fluorotelomers than the C6 phase of Marchetti et al., and ii) when soil is present in the microcosms, it might scavenge the perfluorocarboxylates as well.

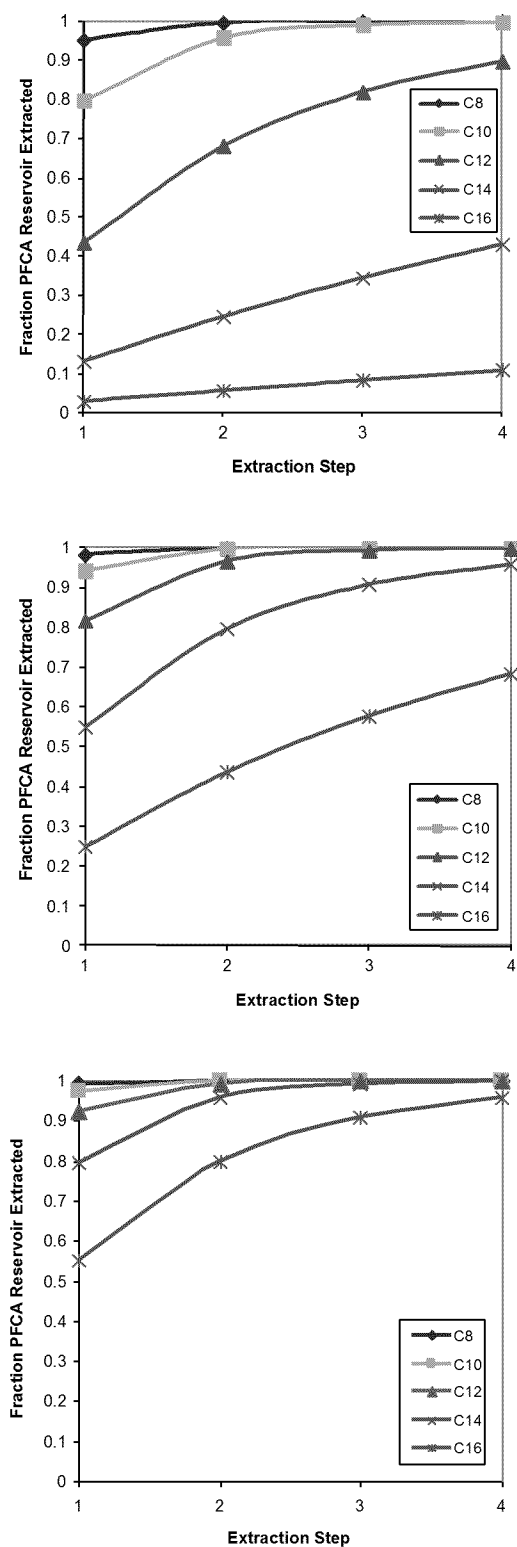


Figure S12A - S12C: Efficacy for extracting perfluorocarboxylates from a proxy FTP using four serial extraction steps with 5 mL of ACN/H₂O per extraction step. A: 60/40; B: 80/20; C: 90/10.

Equations to calculate fluorotelomer- and polyfluoroalkylate-substance (FTSs & PFASs) concentrations in fluorotelomer polymers (FTPs) from analytical concentrations

For FTSs and PFASs extracted from FTPs and FTP microcosms according to our SOP, analyte concentrations can be normalized to FTP-sol basis using the following equations. For FTSs, which are extracted with MTBE and analyzed using GC/MS, concentrations are given by:

$$[\text{Analyte}] = \left(\frac{\text{Analytical Concentration}}{\text{Total Volume of MTBE}} \right) \times \left(\frac{\text{Mass of MTBE in Dilution Step } d+1}{\text{Mass of MTBE in Final Dilution Step } f} \right) \times \left(\frac{\text{Mass of FTP Sol}}{\text{Mass of MTBE in Final Dilution Step } f} \right) \quad (\text{S4})$$

Where:

($\text{Analytical Concentration}$) is the analytical fluorotelomer concentration, ng/mL, in the vial on the GC/MS, f designating final and t for total volume of MTBE in the vial;

(ng $m_{6:2}$) is the nanogram mass of mass-labeled 6:2FTOH, added as a matrix internal standard, in the vial on the GC/MS;

(g $M_{e,t}$) is the total gram mass of MTBE extract;

(ρ_M) is the density of MTBE (g/mL), note that $[(\text{mL } M_{f,t})(\rho_M)]^{-1} = [(g M_{d+1,t}) + (g M_{m_{6:2}})]$;

(g FTP sol) is the gram mass of FTP sol added to the soil-FTP microcosm (at the initiation of the year-long incubation experiment) being subjected to extraction and analysis;

(g $M_{d+1,t}$) is the gram mass of MTBE in dilution step $d+1$, where d designates dilution and t is for total mass, note that for the final dilution step, $d+1$ is replaced by f for final;

(g $M_{d+1,d}$) is the gram mass of MTBE from dilution step d (i.e., the diluted mass) that is added to dilution step $d+1$, note dilution step 1 is designated e for extract; and

(g $M_{m_{6:2}}$) is the gram mass of MTBE stock containing the mass-labeled matrix internal standard $m_{6:2}$ FTOH that is added to the final dilution.

For the LC/MS/MS analytes extracted from microcosms with MTBE, the concentrations of PFASs per unit FTP sol in the microcosm is given by:

$$[\text{PFAS}] = \left(\frac{\text{g A}_{f,t}}{\text{g FTP sol}} \right) \left(\frac{\text{g M}_{e,t}}{\text{g M}_{e,L}} \right) \left\{ \frac{(\text{g A}_{d+1,t})}{(\text{g A}_{d+1,d})} \right\} \quad (S5)$$

Where:

($\text{g A}_{f,t}$) is the analytical polyfluoroalkylate concentration, ng/g, in the vial on the LC/MS/MS, f designating final and t for total volume of ACN in the vial;

(g $\text{M}_{e,t}$) is the total number of grams of MTBE extract;

(g $\text{A}_{r,t}$) is the total gram mass of ACN, containing matrix internal standards, reconstituted in the post-cleanup blow-down vial;

(g $\text{M}_{e,L}$) is the gram mass of MTBE extract dedicated to analysis for polyfluoroalkylates on the LC/MS/MS;

(g FTP sol) is the gram mass of FTP sol added to the soil-FTP microcosm (at the initiation of the year-long incubation experiment) being subjected to extraction and analysis;

(g $\text{A}_{d+1,t}$) is the gram mass of ACN in dilution step d+1, where d designates dilution and t is for total mass, note that: i) for the final dilution step, d+1 is replaced by f for final, and ii) all ACN dilutions for LC/MS/MS analysis contain matrix internal standards; and

(g $\text{A}_{d+1,d}$) is the gram mass of ACN from dilution step d (i.e., the diluted mass) that is added to dilution step d+1, note dilution step 1 is designated r for reconstitution.

For the LC/MS/MS analytes extracted from microcosms with ACN/H₂O, the concentrations of PFASs per unit FTP sol in the microcosm is given by:

$$[\text{PFAS}] = \left(\frac{[\text{PFAS}]_{\text{vial}}}{[\text{ACN}]_{\text{vial}}} \right) \left(\frac{[\text{ACN}]_{\text{vial}}}{[\text{ACN}]_{\text{total}}} \right) \left(\frac{[\text{ACN}]_{\text{total}}}{[\text{FTP sol}]_{\text{total}}} \right) \quad (\text{S6})$$

Where:

$[\text{PFAS}]_{\text{vial}}$ is the analytical polyfluoroalkylate concentration, ng/g, in the vial on the LC/MS/MS, f designating final and t for total volume of ACN in the vial;

$(g A_{r,t})$ is the total gram mass of ACN, containing matrix internal standards, reconstituted in the post-cleanup blow-down vial, note that this value will differ from Equation S5 because it is a separate extraction;

$(g \text{ FTP sol})$ is the gram mass of FTP sol added to the soil-FTP microcosm (at the initiation of the year-long incubation experiment) being subjected to extraction and analysis;

$(g A_{d+1,t})$ is the gram mass of ACN in dilution step $d+1$, where d designates dilution and t is for total mass, note that: i) for the final dilution step, $d+1$ is replaced by f for final, and ii) all ACN dilutions for LC/MS/MS analysis contain matrix internal standards; and

$(g A_{d+1,d})$ is the gram mass of ACN from dilution step d (i.e., the diluted mass) that is added to dilution step $d+1$, note dilution step 1 is designated r for reconstitution.

Disclaimer: The residual and impurity species we report in Table S1, as well as all of our publically accessible research reported herein and elsewhere, were selected based on previous publications as well as potential-toxicity concerns. When we identified a specific chemical species as present in a sample, our practice was to search for homologues of the species over the range of C6 through C16 at a minimum. None of the chemical species we report were selected based on confidential business information. The values we report are residual, impurity, and/or degradation-product concentrations that are extractable by the methods we describe and not intended to represent the structural composition of the tested polymers. Data presented in Figure 3 were selected because they were among the higher-concentration analytes.

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